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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

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ON THE

PROGRESS OF CHEMISTRY

FOR 1914.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.*
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. applicata	Annali di Chimica Applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann Physik.	Annalen der Physik.
Ann. Report	Annual Reports of the Chemical Society.
Arch. Pharm.	Archiv der Pharmazie.
Arkiv. Kem. Min. Geol.	Archiv för Kemi. Mineralogi och Geologi.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Biochem. Bull.	Biochemical Bulletin.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. Chim. Farm.	Bolletino chimico farmaceutico.
Bot. Zentr.	Botanisches Zentralblatt.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci., St. Pétersbourg	Bulletin de l'Academie Impériale des Sciences de St. Pétersbourg.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Chem. and Drug.	Chemist and Druggist.
Chem. News	Chemical News.
Chem. Rev. Fett. Harz.-Ind.	Chemische Revue über die Fett.-und Harz.-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Deutsch. med. Wochensch.	Deutsche medizinische Wochenschrift.
Gazzetta	Gazzetta chimica italiana.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Chim. Phys.	Journal de Chimie physique.

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* The year is not inserted in references to 1914.

ABBREVIATED TITLE.	JOURNAL.
J. Coll. Sci. Tōkyō	Journal of the College of Science, Tōkyō.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Hygiene	Journal of Hygiene.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing.	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys.	Journal de Physique.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
Kolloid. Zeitsch.	Kolloid-Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. Zentr.-h.	Pharmaceutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
P.	Proceedings of the Chemical Society.
Proc. Amer. Acad.	Proceedings of the American Academy.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Physical Soc. London.	Proceedings of the London Physical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Archiv. Physiol.	Skandinavisches Archiv. für Physiologie.
South African J. Sci.	South African Journal of Science.
T.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Gärungsphysiol	Zeitsch. für Gärungsphysiologie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie and Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

The custom of reporting on a few only of the many available topics has been adhered to.

Although no revolutionary discovery has been made, progress on the old lines has been rapid. Unless all signs are misleading, the so-called anomalies of strong electrolytes and of conducting solutions in general are on the point of being explained. In the correlation of the physical properties of substances, and in the determination of the dependence of these on the constitution and structure of the molecules, notable advances have been made. The once hypothetical atoms continue to assume more of the features of reality. In a period covered by not much more than ten years, the masses of single atoms have been determined accurately by half-a-dozen independent methods, and recently a knowledge of their structure, as deduced from modern electrical research, has enabled the calculation of many of their natural periods of vibration to be performed. The last achievement has been made possible by the adoption of the principle, known as Planck's quantum law. Stated in a simple form, the law is this: particles of matter emit and absorb energy not slowly and continuously, but in "jerks." In other words, the process of emission of energy is assumed in all cases to be analogous to the process which occurs when a molecule changes into an isomeric form. The latter process has always been assumed by chemists to be a sudden one, and therefore accompanied by a sudden evolution of energy. Planck's hypothesis, therefore, is equivalent to the assertion that all energy changes in matter are of the same character as those which occur in chemical change. The discontinuous character of all chemical change has become so familiar to chemists that it has ceased to be regarded as strange, or as needing explanation. Yet Planck's generalisation is considered by some physicists to involve the abandonment of the principle—*Natura non facit saltum*—and the denial of the continuity of dynamical effect.

The magnitudes of the finite quantities of energy, or, as they are called, quanta, emitted or absorbed when particles of matter change their state are, in order to account for the general laws of radiation, assumed to be related to the vibration-frequency of the energy. From the laws of radiation it can be shown that the relation is the extremely simple one: the vibrational frequency of the energy of a quantum is directly proportional to the magnitude of the quantum. It was calculated by Planck from the total radiation from unit surface of heated platinum that the constant, h, by which the frequency must be multiplied to give the quantum, is $6{\cdot}55 \,.\, 10^{-27}$ erg. sec.

The Specific Heats of Solids.[1]

If the atoms of a solid be regarded as rigid points vibrating about fixed positions of equilibrium, and acted on by forces proportional to the displacements from the positions of equilibrium, the average energy of each atom should, according to classical dynamics, be given by the expression $3kt$, and the specific heat of an atom by $3k$, k being the value of pv/t for a single molecule of a perfect gas. Therefore, on the above hypothesis as to the structure of solids, the atomic heat of an elementary substance ought always to be equal to $3R$ or $5{\cdot}95$ cals., a deduction which is in accordance with the law of Dulong and Petit. Furthermore, Nernst and his collaborators have shown that the agreement is still closer at the ordinary temperature if the atomic heats are calculated from the specific heats at constant volume.[2]

At lower temperatures, however, the relation of Dulong and Petit ceases to hold, the atomic heats of all the elementary substances being much lower than at the laboratory temperature, and probably vanishing entirely at the absolute zero. This diminution in the atomic heats with decreasing temperature can be readily shown to be a direct consequence of the quantum law. Planck[3] has deduced that the energy of an electromagnetic resonator of frequency v, in equilibrium with black body radiation of temperature t, is given by the expression $kt\dfrac{\frac{hv}{kt}}{e^{\frac{hv}{kt}}-1}$. The energy of such a resonator, deduced on the assumption that the ordinary dynamical principles hold, is kt. Accordingly, to obtain the energy of a vibrator, we must multiply the energy as deduced from the principle of equipartition of kinetic energy (which is a consequence of classical dynamics) by the factor $\dfrac{\frac{hv}{kt}}{e^{\frac{hv}{kt}} - 1}$.

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[1] See *Ann. Reports*, 1912 and 1913.

[2] W. Nernst and F. A. Lindemann, *Zeitsch. Elektrochem.*, 1911, **17**, 817; *A.*, 1911, ii, 1059.

[3] Planck deduces this formula with the aid of the theory of probability. It can,

By precisely similar reasoning, Einstein has deduced that the energy of an atom of a solid must be given by $3kt\dfrac{\frac{hv}{kt}}{e^{\frac{hv}{kt}} - 1}$, instead of by $3kt$, as demanded by the classical dynamics. In the above formula, v is the characteristic vibration period of the atom, which in the case of transparent crystals is the frequency of the residual radiation. The weakness of the formula is that it implies that an atom of a solid element has but one characteristic period of vibration. The differentiation of the expression with respect to t gives of course the specific heat of the atom.

Nernst and Lindemann,[4] with what appears to be insufficient

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however, be much more easily deduced from the well-known thermodynamic formula of van't Hoff

$$\frac{Q}{Rt^2} = \frac{d \log_e K}{dt}$$

in the following way.

Assume that resonators of vibration period v are attached to the molecules of a gas. By the quantum law, there will be vibrators possessing amounts of energy given by $o, hv, 2hv, \ldots$ etc., but no vibrators with intermediate amounts of energy. Let the number of vibrators with $o, hv, 2hv, \ldots$ etc. amounts of energy be $n_0, n_1, n_2, \ldots$ etc. respectively. Then by van't Hoff's equation

$$\frac{mhv}{kt^2}dt = d \log_e \frac{n_m}{n_0}.$$

From this equation it follows, by integration with respect to t between $t = t$ and $t = \infty$, that

$$n_m = n_0 e^{\frac{-mhv}{kt}}$$

and therefore the mean energy of a vibrator is given by

$$\frac{hve^{\frac{-hv}{kt}} + 2\,hve^{\frac{-2hv}{kt}} + 3hve^{\frac{-3hv}{kt}} + \ldots \text{ etc.}}{1 + e^{\frac{-hv}{kt}} + e^{\frac{-2hv}{kt}} + \ldots \text{ etc.}}$$

which reduces to $\dfrac{hv}{e^{\frac{hv}{kt}} - 1}$.

When kt is large in comparison with hv, the above expression for the mean energy of a vibrator is approximately kt, which is the value deduced from the classical kinetic theory.

[4] *Ann. Report*, 1912.

theoretical justification, add another term to Einstein's formula for the specific heat.

P. Debye[5] has deduced an expression for the energy of an atom of a solid elementary substance, which is:

$$E = \int_0^{v_m} \frac{9hv^3 dv}{v_m{}^3\left(e^{\frac{hv}{kt}} - 1\right)}.$$

In deriving this formula, he assumes that the solid vibrates as a whole, and that the vibration-frequencies can assume any value from 0 to v_m, the energy of frequencies greater than v_m being negligible. He also assumes that the energy of the vibrations is equal to the amounts assigned to them by the quantum principle. He shows how v_m can be calculated from the elastic constants of the solid. As mentioned in last year's Report, Debye's formula is in better accord with the facts than those of Einstein, and Nernst and Lindemann. It is a little surprising that the values of v_m in Debye's formula, calculated from the elastic constants in accordance with the theory, do not give such satisfactory calculated values of the atomic heats as values of v_m obtained from an empirical formula proposed by Lindemann.[6]

With the view of testing the three theoretical formulæ for the atomic heats of the elements, E. H. Griffiths and E. Griffiths[7] have determined with great accuracy the specific heats of the metals aluminium, copper, zinc, silver, cadmium, lead, iron, and sodium by their method of cooling over a range of temperature extending from 120° A. to 400° A. In principle, the experimental method consists in measuring (*a*) the amount of heat that must be supplied to a metal block in unit time in order to maintain a constant difference of temperature between the enclosure and the metal, and (*b*) the rate of cooling of the metal block for the same difference of temperature between the enclosure and the metal. The enclosure was kept at a low temperature by means of cold air (cooled by expansion through a jet) circulated through an enveloping metal coil. Heat was supplied to the metal block at a constant rate by the passage of an electric current through a known resistance embedded in the metal.

The comparison with the formulæ was made in each case by selecting values of v and v_m which made the locus of the specific heat-temperature curve coincide most closely with the corresponding theoretical curve at the lower temperatures. It was thus shown that none of the theoretical formulæ is capable of representing the results over the entire range of temperature.

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[5] *Ann. Physik*, 1912, [iv], **39**, 739; *A.*, 1912, ii, 1134.

[6] *Physikal. Zeitsch.*, 1910, **11**, 609.

[7] *Phil. Trans.*, 1914, [*A*], **214**, 319; *A.*, ii, 798.

The discrepancies in most cases were greatest at the position where the radius of curvature is greatest. In the case of sodium, the atomic heat at 365° A. was 7·43, as compared with 6·44 calculated from Debye's formula.

Several valuable papers dealing with the experimental determination of the specific heats of solids,[8, 9] and the closely allied subject of the electrical resistance of metals at very low temperatures[10] have appeared.

The Structure of Atoms. The Interpretation of the Line Spectra of the Elements. The X-ray Spectra of the Elements.

Without doubt the most striking investigations of the last two years have been those in which Rutherford's[11] model of the atom and Planck's quantum hypothesis have been employed to interpret the line spectra of the elements. According to Rutherford, an atom consists of a central positively charged nucleus, the diameter of which is at least one hundred thousand times less than that of a complete atom. The positively charged nucleus is surrounded by a planetary system of negative electrons. On this view, the central nucleus, in spite of its minute dimensions, contains almost the whole mass of the atom and an excess positive charge of a definite number of positive electrons. The number of positive electrons in excess of the negative electrons on the central nucleus is by some authorities supposed to be the same as the number of the element in the periodic table, and is known as the atomic number.[12] The chemical properties and even the spectra of the elements appear to depend almost entirely on the atomic number.

Bohr's Theories of the Line Spectrum.

In a series of papers published at intervals during the latter half of 1913 and this year, N. Bohr,[13] with the aid of Rutherford's model of the atom and the quantum principle, has attained remarkable success in accounting for the series spectra of hydrogen and helium.

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[8] E. Griffiths, *Proc. Roy. Soc.*, 1914, [*A*], **89**, 561 ; *A.*, ii, 245.

[9] W. Nernst and E. Schwers, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 355 ; *A.*, ii, 337.

[10] H. K. Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 673 ; *A.*, ii, 163. Compare *A.*, 1913, ii, 748, 822.

Phil. Mag., 1911, [vi], **21**, 669 ; 1914, [vi], **27**, 488 ; *A.*, 1911, ii, 453 ; 1914, ii, 323.

[12] A. van den Brock, *Nature*, 1913, **93**, 373, 476 ; F. Soddy, *Ann. Report*, 1913, 271.

[13] *Phil. Mag.*, 1913,]vi], **26**, 1, 476 ; 1914, [vi], **27**, 506 ; *A.*, 1913, ii, 689, 943.

The hydrogen atom is regarded as a central nucleus charged with an atom of positive electricity and having a negative electron rotating round it in an orbit determined by the electrostatic attraction of the charges and the ordinary laws of motion. In his last paper, Bohr demonstrates that the same results are obtained for an elliptic as for a circular orbit. We may, therefore, for simplicity consider only the special case of a circular orbit. From the classical mechanics it can be deduced that:

$$W = \frac{e^2}{2a} \text{ and } \omega^2 = \frac{2W^3(M+m)}{\pi^2 e^4 m M},$$

in which W is the energy required to remove the electron to infinity, e the charge of an electron, a the radius of the orbit, m the mass of the electron, M the mass of the central nucleus, and ω the frequency of revolution. These equations impose no limitation on the values of ω, and accordingly, if the motion of the electron is controlled entirely by the laws of Newtonian mechanics, the atom can only emit a continuous spectrum. In other words, the line spectrum can only be accounted for by assuming the operation of some principle which restricts the values of ω to definite magnitudes. The principle assumed by Bohr is that $2W$ must be a definite multiple of $h\omega$, h being Planck's constant. The analogy between this assumption and that of Planck, namely, that twice the mean kinetic energy of a resonator of period v is a definite multiple of hv, is, as Bohr points out, complete. Bohr's principle limits the magnitudes of W to the values of the expression:

$$\frac{2\pi^2 e^4 m M}{n^2 h^2 (M+m)},$$

in which n is a whole number.

The possible orbits are accordingly characterised by the whole numbers from 1 to ∞, and if the orbit changes from that corresponding with $n=n_1$ to that corresponding with $n=n_2$, an amount of energy equal to $\frac{2\pi^2 e^4 m M}{h^2(M+m)}\left(\frac{1}{n_2{}^2} - \frac{1}{n_1{}^2}\right)$ will be emitted.

Bohr assumes further that this emitted energy is exactly one quantum; so that, if the period of the radiation is v,

$$v = \frac{2\pi^2 e^4 m M}{h^3(M+m)}\left(\frac{1}{n_2{}^2} - \frac{1}{n_1{}^2}\right).$$

Now the Balmer series for hydrogen is given by:

$$v = N\left(\frac{1}{2^2} - \frac{1}{n^2}\right);$$

the Paschen series by:

$$v = N\left(\frac{1}{3^2} - \frac{1}{n^2}\right),$$

and the recently discovered Lyman series by:

$$v = N\left(\frac{1}{1^2} - \frac{1}{n^2}\right).$$

Accordingly, if the numerical values of the spectroscopic constant N and $\frac{2\pi^2 e^4 m M}{h^3(M+m)}$ are the same, Bohr's theory is in accord with the observed facts. The actual value of N is $3{\cdot}29 \times 10^{15}$, whereas the calculated value of Bohr's constant, using the most trustworthy values of m, e, and h, is $3{\cdot}26 \times 10^{15}$.

The Helium Spectrum.—The most striking confirmation of Bohr's theory is afforded by a newly discovered series of lines belonging to the spectrum of helium. Two years ago, A. Fowler[14] observed this series of lines in the spectrum of a mixture of hydrogen and helium. The lines are given by the general formula:

$$4N\left(\frac{1}{3^2} - \frac{1}{n^2}\right).$$

These lines were at the time attributed to hydrogen owing to the close relationship of the formula giving their frequencies to the formula for Balmer's series. They can, however, according to Bohr's theory, be given by a helium atom which has lost one of its two electrons, and Fowler, from strong evidence obtained independently, now holds the view that these lines must belong to the helium spectrum, as suggested by Bohr. Moreover, J. Stark[15] has found that the line λ 4686 (the principal line in the above series) was emitted during the spark discharge through a helium tube which showed no trace of the hydrogen spectrum in any circumstances. Furthermore, the N of this series differs slightly from the N of Balmer's series, as it should, in accordance with the theory, owing to the mass of the nucleus of helium being four times that of hydrogen. Again, from the observed ratio of the two N's the ratio of the mass of the hydrogen atom to that of the electron can be calculated, and has been found by Fowler[16] to be 1836, a number in extraordinarily good agreement with that given by the best determinations of the constant.

Other lines observed by Nicholson in the spectra of the stars are now on the evidence of Bohr's hypothesis assigned to helium and lithium.

It should here be mentioned that W. E. Curtis[17] has recently measured with extreme accuracy the first six lines of the series spectrum of hydrogen, and from his results arrives at the conclusion that Balmer's formula does not afford an exact representation of the wave-lengths of the lines. The modified formula derived by Curtis is:

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[14] *Monthly Notices, Royal Ast. Soc.*, 1912, December, 73.

[15] *Ber. Deut. physikal. Ges.*, 1914, **16**, 468; *A.*, ii, 50.

[16] *Phil. Trans.*, 1914, [*A*], **214**, 225.

[17] *Proc. Roy. Soc.*, 1914, [*A*], **90**, 605; *A.*, ii, 761.

$$v = \frac{N}{4} - \frac{N}{(m+\mu)^2},$$

in which $N = 109679{\cdot}22$ and $\mu = 0{\cdot}0000069$. The departure from Balmer's formula is therefore very slight.

The X-ray Specira of the Elements.—When the metals are bombarded by the cathode rays they emit continuous spectra and line spectra of X-radiation. The radiation of any line can be reflected from the face of a crystal only at a definite angle. From the magnitude of the angle of reflection the frequency of the line can be calculated by a simple formula. The method of analysing X-radiation by reflection from the surface of a crystal was developed by W. L. and W. H. Bragg.[18]

H. G. J. Moseley[19] has systematically examined the X-ray spectra of the elements from aluminium to gold. He finds that the X-ray spectra emitted by the elements contain corresponding lines, and that the frequencies of the corresponding lines are given by the general formula:

$$v = A(N-b)^2,$$

in which A and b are constants, the same for all the elements, and N is a whole number which characterises the element, and is identical with the number of the position of the element in the periodic table. For two of the lines, $K\alpha$ and $L\alpha$, A is given very closely by the expressions $\left(\frac{1}{1^2} - \frac{1}{2^2}\right)v_0$ and $\left(\frac{1}{2^2} - \frac{1}{3^2}\right)v_0$, in which v_0 is the Rydberg constant, and very nearly equal to Bohr's constant:

$$\frac{2\pi^2 e^4 m M}{h^3(m+M)}.$$

The constant b for the lines measured is less than one. A single electron revolving round a nucleus of charge Ne should, according to Bohr's theory, emit radiation of frequency $v_0\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)N^2$. Moseley advances the hypothesis that the X-ray lines arise from the rotation of several electrons round the central nucleus, and that b is a small term arising from the influence of the n electrons in the ring on each other.

As J. W. Nicholson[20] has pointed out, Moseley's theory implies a modification in Bohr's original hypothesis, since the assumption is made that in the passage of the atom from one stationary state to another each electron in the ring evolves one quantum of energy, whereas Bohr's theory definitely stipulates that in such a change only one quantum of energy is radiated from the atom.

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[18] *Ann. Report*, 1913, 239.

[19] *Phil. Mag.*, 1913, [vi], **26**, 1033; 1914, [vi], **27**, 703; *A.*, ii, 14, 326.

[20] *Ibid.*, 1914, [vi], **27**, 563; *A.*, ii, 325.

What is certainly established by Moseley's work is that the *X*-ray spectra of the elements depend on the atomic number, and not on the atomic weight; for example, in the list of the elements arranged according to their *X*-ray spectra, cobalt and nickel do not appear in the order of their atomic weights, but in the order which must be assigned to them from a consideration of their chemical properties.

Properties of Liquids and their Saturated Vapours: Latent Heats of Vaporisation.

Considerable activity has been displayed during the year in attempts to discover relations between the physical properties of liquids and those of their saturated vapours. Several new formulæ for the latent heat of vaporisation have been proposed.

In 1902, J. E. Mills[21] expressed the view that the internal heat of vaporisation, that is, the difference between the heat of vaporisation and the external work performed during evaporation is equal to the work done against molecular attraction in separating the molecules. He also assumed that molecular attraction between two molecules is inversely proportional to the square of the distance between the molecules[22] and independent of the temperature. From these hypotheses he deduced the formula:

$$L = E + \mu(d_1^{\frac{1}{3}} - d_2^{\frac{1}{3}}),$$

E being the external work, μ a constant, and the suffixes 1 and 2 referring to the liquid and vapour respectively. The formula undoubtedly corresponds very closely with the facts.[23]

J. Kendall[24] has recently shown that the density of a liquid and that of its saturated vapour can both be represented accurately by simple empirical formulæ involving only the critical constants, the temperature, and a constant peculiar to the substance. His expressions for the densities of the liquid and vapour are respectively:

$$d_1^{\frac{1}{3}} - d_c^{\frac{1}{3}} = k_1(t_c - t)^{\frac{1}{3}},$$

and

$$d_c^{\frac{1}{3}} - d_2^{\frac{1}{3}} = k_2(t_c - t)^{\frac{1}{2}},$$

the suffix c referring to the critical point.

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[21] *J. Physical Chem.*, 1902, **6**, 209 ; *A.*, 1902, ii, 596.

[22] The force of cohesion cannot follow the law of the inverse square of the distance strictly ; for, if such were the case, the internal pressure would not be almost constant throughout the body of the liquid, and variable only at the surface.

[23] *J. Physical Chem.*, 1906, **10**, 1 ; *A.*, 1906, ii, 216.

[24] *Medd. K. Vet. Nobelinstitut*, 1913, **2**, No. 29 ; *A.*, ii, 101.

If the values for d_1 and d_2 obtainable from these formulæ are substituted in Mills' expression for the latent heat, the equation:

$$L = E + k_1\mu(t_c - t)^{\frac{1}{3}} + k_2\mu(t_c - t)^{\frac{1}{2}}$$

is obtained, and this is again closely in accord with the facts. At low temperature, since the density of the vapour is negligible in comparison with that of the liquid, the above equation reduces to:

$$L = \frac{Rt}{M} + k_1\mu(t_c - t)^{\frac{1}{3}} + \mu d_c^{\frac{1}{3}},$$

and the necessary consequence of Nernst's theory of chemical energy that $\frac{dL}{dt} = 0$ is fulfilled if $k_1\mu M = 3Rt_c^{\frac{2}{3}}$. The latter relation is found to be satisfied by normal liquids.

It is noteworthy that the above equations, which give the densities of the liquid and vapour in terms of the temperature, the critical density, and the critical temperature, are inconsistent with the law of the rectilinear diameter.

Kendall finds that the heat of vaporisation is given with a fair degree of accuracy by the simpler formula:

$$L = k(t_c - t)^{0{\cdot}386}.$$

The above formulæ are not applicable to associated liquids. Of the associated liquids water, methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid, water and methyl alcohol depart the least and acetic acid the most from the behaviour of normal liquids.

D. Tyrer[25] has advanced an empirical expression for the latent heat of vaporisation differing slightly from the simple formula proposed by Kendall.

Twenty years ago G. Bakker[26] deduced, as a necessary consequence of van der Waals' assumption that the total pressure of a fluid is given by the formula $\pi = \frac{Rt}{v - b}$, the expression $Rt \log_e \frac{v_2 - b}{v_1 - b}$ for the latent heat of vaporisation. The values of the latent heats calculated from the formula are in most cases more than 20 per cent. below the experimentally determined magnitudes. Only in the case of the monatomic mercury is the formula found to be in accord with the facts. Therefore van der Waals' expression for the total pressure of a fluid is (except for substances the molecules of which are monatomic) inaccurate if b is taken as constant.

If b is assumed to vary with the temperature only, M. P. Applebey and D. L. Chapman[27] have shown that the expression for the latent heat becomes:

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[25] *J. Physical Chem.*, 1913, **17**, 717; *A.*, ii, 102.

[26] *Zeitsch. physikal Chem.*, 1895, **18**, 519.

$$Rt \log_e \frac{v_2 - b}{v_1 - b} + Rt^2\left(\frac{1}{v_1 - b} - \frac{1}{v_2 - b}\right)\frac{db}{dt}.$$

If b is assumed to be a linear function of the temperature, the agreement between the experimentally determined latent heats and the values calculated from the above expression is, for non-associated substances, close. Furthermore, the "coefficient of expansion" with temperature of b is found to be approximately the same for all non-associated substances. Of the associated substances, methyl alcohol, ethyl alcohol, propyl alcohol, and acetic acid, methyl alcohol departs the least, and acetic acid the most, from the behaviour of normal substances. As already mentioned, Kendall, with the aid of his empirical formula, arrived at the same conclusion. In deducing the last-mentioned formula for the latent heat of vaporisation, the assumption was made that b is a function of the temperature only, that its value is independent of the pressure, and that it therefore has the same magnitude in the liquid and the gaseous phases. The assumption will require justification, since it is apparently at variance with Richards' views on the compressibility of the atoms.

T. W. Richards[28] has published an interesting non-mathematical discussion of the significance of the quantity b in van der Waals' equation. Apart from its intrinsic interest, the paper is of value in that it contains many references to earlier work on the subject. The author draws the conclusion that, for carbon dioxide at 1·15° above the critical temperature, b is nearly constant until the gas is compressed to the critical volume, and that it then diminishes rapidly as the pressure is further increased. His comment on this striking conclusion is: "There is no evident reason why b should change over a wide range of pressure until one reaches the neighbourhood of the bulk of b itself, whether the molecules are compressible or not. On the other hand, the sudden decrease of b under high pressure (when the volume of the gas has been brought almost down to the bulk of b itself) may indicate that then the entity represented by b is really being compressed." He examines the data for the compressibility of helium and hydrogen at different temperatures and arrives at the remarkable conclusion that b for the former gas has a negative temperature coefficient of expansion. The author is careful to state that the calculated values of the temperature-coefficient of expansion and the compressibility of b are dependent on the assumptions made as to the nature of the forces of cohesion. J. J. van Laar[29] has also discussed the deviations from van der Waals' ideal equation of condition, and has put forward the view that these deviations are due to the variability of the quantity b with the volume and with the temperature. He has shown what conclusions can be drawn from the assumption that b is a function of the volume. He has obtained some evidence for the view that the variation of b with temperature is very slight at higher temperatures, but that it increases as the temperature falls.

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[27] *T.*, 1914, **105**, 734.

[28] *J. Amer. Chem. Soc.*, 1914, **36**, 617; *A.*, ii, 340.

In a later paper[30] the same author arrives at conclusions which, if they can be confirmed by further research, will considerably simplify the problem of finding a general characteristic equation for non-associated fluids. In the first place, he concludes that the quantity a in van der Waals' equation is independent of the density over a very large range of volume. In other words, at the same temperature the molecular attraction in both the gaseous and the liquid states can be satisfactorily represented by the expression a/v^2. In the second place, he advances arguments for the view that the quantity b is the volume occupied by the molecules and not, as van der Waals endeavoured to show, four times this magnitude. That in liquids at low temperatures the quantity b cannot be much greater than the volume of the molecules is evident from the circumstance that the density of the liquid is not much smaller than the density of the substance at a temperature very near to the absolute zero, when the molecules must be almost in contact with one another.

It has been shown that the volume of a molecule as calculated from the critical constants is approximately the sum of the volumes of the constituent atoms.[31] The volume of an atom is, however, dependent to some extent on constitutive influences. Thus the volume of molecules for cyclic compounds, calculated from the atomic volumes derived from a consideration of saturated compounds, is larger than the volume obtained directly from the critical constants.

The Compressibility of Liquids.

Amongst the data most needed for the elucidation of the nature of cohesion and the determination of the so-called "effective collision-bulk" of the molecules are accurately determined values of the compressibility of liquids.

D. Tyrer[32] has recently completed an investigation of the

[29] *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 808; *A.*, ii, 341.

[30] *Ibid.*, **17**, 451; *A.*, ii, 801.

[31] J. D. van der Waals, *ibid.*, **16**, 880; *A.*, ii, 342.

[32] *T.*, 1913, **103**, 1675; 1914, **105**, 2534.

adiabatic compressibility of several of the liquids, the physical properties of which have been most carefully examined in other respects. The method he adopts is simple, and apparently capable of furnishing results the maximum error of which does not exceed 0·5 per cent. of the determined constant. The liquid is contained in a globe provided with a horizontal graduated capillary tube. Beyond the liquid the capillary tube contains a thread of mercury which prevents evaporation. To eliminate a correction due to the deformation of the globe, the pressure is applied simultaneously to the inside and outside. On releasing the pressure, the alteration in volume can be obtained from the movement of the liquid meniscus in the capillary tube. The only correction which it is necessary to apply is that due to the hydrostatic adiabatic compressibility of the glass. Numbers in excellent accord with one another were obtained with a glass and a copper globe.

The isothermal compressibility was deduced from the adiabatic compressibility with the aid of the thermodynamic formula:

$$\beta = a + \frac{T\left(\frac{dv}{dt}\right)^2}{JvC_p},$$

in which β and a are the isothermal and the adiabatic compressibilities respectively, and the other symbols have their usual significance. The values of $\frac{dv}{dt}$ were obtained from Young's extensive experimental data, and those of C_p from several sources. The investigation discloses the fact that a large number of compressibility data published by numerous authors as isothermal are in reality adiabatic, whereas other values, especially those obtained by the application of higher pressures, are intermediate between the true adiabatic and isothermal values. There can, in fact, be no doubt that many previous investigators, amongst whom Quincke must be included, have ignored the effect of the rise of temperature which occurs when a liquid is suddenly compressed. Tyrer quotes a number of compressibilities, published by Quincke as isothermal, which differ but little from the true adiabatic compressibilities, but are, in most cases, as much as 40 per cent. below the true isothermal compressibilities.

In conjunction with Young's determinations of the vapour pressure and of the densities of the liquid and vapour phases, Tyrer's values of the compressibility will materially assist in deducing the form of the general characteristic equation of fluids, and it is to be hoped that the author will extend his investigations to temperatures considerably above the boiling point—if possible to the critical temperature.

Relations between the Physical Properties of Pure and Mixed Liquids.

The relations which have been observed between the specific inductive capacity and the latent heat[33] and internal pressure[34] of liquids have been further investigated by W. C. M. Lewis.[35]

An exact and simple relation between the vapour pressure and surface tension of mixtures of liquids has been discovered.[36]

Optical and Magnetic Rotatory Dispersion.

The accumulation of data relating to the phenomena of optical and magnetic rotation during the last three or four years has been so immense that it is only possible in this short review to indicate, in the broadest outline, the advances which have been made in our knowledge of the more general problems that have arisen out of the labours of the numerous investigators, in this fertile field of research.

Biot who, in 1815, discovered the property of optical rotatory power, observed that in general the rotation which the polarised ray experienced in its passage through the active material was greater the shorter the wave length; but that there were exceptions to the rule, a notable case being that of tartaric acid in solution. It was this observation that led to the distinction being made between "normal" and "anomalous" rotatory dispersion. The dispersion ratios $\frac{[\alpha]_F}{[\alpha]_C}$ of compounds of the former class vary between the limits 1·8—2·0, and are not, as a rule, altered to an appreciable extent by rise of temperature or dissolution. Hydrocarbons, most alcohols, sucrose, and quartz belong to this class of substances.

The rotation and the dispersion of the second class of substances are, however, considerably influenced by the temperature and the nature of the solvent, and therefore a substance that exhibits anomalous dispersion under some conditions may show normal dispersion under other conditions. Those substances which behave normally under all conditions are classified as normal. There is reason to believe that in the extreme ultra-violet or ultra-red all substances would exhibit anomalous dispersion.

There can be little doubt that anomalous dispersion can arise from two causes:

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[33] E. Obach, *Phil. Mag.*, 1891, [v], **32**, 113; *A.*, 1892, 258.

[34] P. Walden, *Zeitsch. physikal. Chem.*, 1909, **66**, 407; *A.*, 1909, ii, 547.

[35] *Phil. Mag.*, 1914, [vi], **28**, 104; *A.*, ii, 625.

[36] R. P. Worley, *T.*, 1914, **105**, 206, 273.

(*a*) From the existence of at least two strong absorption bands in the spectrum of the substance under examination.

(*b*) From the substance consisting of a mixture of different kinds of normally dispersing molecules differing in rotatory dispersion as well as in the sign of their rotation.

Biot prepared such mixtures, and Arndsen in 1858 advanced the hypothesis that the abnormality of tartaric acid was due to this cause.

The Ionic Theory of Optical and Magnetic Rotatory Dispersion.

A theory which has proved of inestimable value in the interpretation of the phenomena of optical and magnetic rotation is the electron hypothesis of Drude.[37] In the development of the theory, the same assumptions are made as those postulated in the well-known theory of ordinary dispersion, together with the assumption that the free electrons are, on account of their being situated in an isotropic unsymmetrical medium, constrained to move in short helices twisted in the same direction with axes directed at random in space instead of in short, straight lines. The theory leads to the formula:

$$\alpha_\lambda = \Sigma \frac{k_n}{\lambda^2 - \lambda_n{}^2},$$

in which α_λ is the rotation for the wave-length λ, k_n is a constant, and λ_n the wave-length corresponding with the frequency of the vibrating electron. In the above series, each term gives the magnitude of the effect of a single electron in the molecule on the rotation; so that, if a molecule contains n electrons vibrating with different frequencies, the complete characteristic equation of a substance composed of such molecules must contain n terms. It is important not to lose sight of the possibility that a single electron in a molecule may have more than one period of vibration.

Experimental Evidence of the Validity of Drude's Formula.

The experimental evidence of the validity of Drude's formula rests principally on determinations of the rotatory dispersion of quartz. It was with measurements of the rotatory power of this substance that Drude originally tested his theory.

Two years ago, T. M. Lowry[38] published the results of six years' labour on the optical and magnetic rotation of quartz, and the work has since been continued in collaboration with T. W. Dickson.[39] The chief result of these investigations has been to show that the rotatory power of quartz from the wave-length 16,740 to the wave-length 2327 is given with a maximum error of less than 1 part in 25,000 by the formula

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[37] "The Theory of Optics," 1907.

[38] *Phil. Trans.*, 1912, [*A*], **212**, 261.

[39] *Trans. Faraday Soc.*, 1914, **10**, 96; *A.*, ii, 786.

$$\alpha = \frac{k_0}{\lambda^2 - \lambda_0{}^2} + \frac{k_1}{\lambda^2 - \lambda_1{}^2} + \frac{k_2}{\lambda^2 - \lambda_2{}^2}.$$

The results must evidently be regarded as striking confirmation of Drude's theoretical deductions.

Normal Rotatory Dispersion.

Considered in the light of Drude's theory, the cause of the difference between "normal" and "anomalous" substances becomes more intelligible. Simple organic liquids, sucrose, quartz, etc., which belong to the first class, and for which the ratio $\frac{[\alpha]_F}{[\alpha]_C}$ in all circumstances is not outside the limits 1·8—2·0, are substances that have one or more predominating natural periods of vibration of the same sign in the ultra-violet. The optical and magnetic rotation of light in the visible spectrum for such substances can be represented with a sufficient degree of accuracy by the one-term formula

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2},$$

which clearly makes $\frac{[\alpha]_F}{[\alpha]_C} = \frac{\lambda_C^2 - \lambda_0^2}{\lambda_F - \lambda_0^2} \bumpeq \frac{\lambda_C^2}{\lambda_F^2}.$ To avoid the ambiguities which arise from the use of the terms "normal" and "anomalous dispersion," Lowry proposes to distinguish between *simple rotatory dispersion*, which can be expressed by an equation with only one term, and *complex rotatory dispersion*, which requires for its complete expression an equation containing at least two terms. In making this classification, it is of course realised that the distinction only applies to a limited range of wave-lengths, and that even for this limited range the single-term formula could not express the rotatory dispersions within the limits of experimental error if the measurements could be made with the degree of accuracy which has been attained in the case of quartz. As might be expected, substances that exhibit simple rotatory dispersion are those which are most devoid of "colour" at the least refrangible end of the ultra-violet. It has been shown by T. M. Lowry and T. W. Dickson[40] that the rotatory dispersion of a large number of organic compounds in the homogeneous state can usually be expressed by the single-term formula, and T. M. Lowry, R. H. Pickard and J. Kenyon[41] have shown that the simpler carbinols previously examined by Pickard and Kenyon follow the simple law at a temperature of 20°. The degree of concordance with which the formula fits the facts is illustrated by the following table, taken from the paper by Lowry and Dickson:

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[40] *T.*, 1913, **103**, 1067.

[41] *Ibid.*, 1914, **105**, 94.

	Red.		Yellow.	Green.		Blue.		Violet.
	Li 3708.	Cd 6438.	Na 5893.	Hg 5461.	Cd 5086.	Cd 4800.	Cd 4678.	Hg 4359.
sec.-Amyl alcohol......	0·642	—	0·846	1·000	—	—	—	1·652
sec.-Hexyl ,, ...	0·639	—	0·847	1·000	1·169	1·331	—	1·653
sec.-Heptyl ,, ...	0·638	—	0·847	1·000	—	—	—	1·648
sec.-Octyl ,, ...	0·640	0·699	0·847	1·000	1·169	1·329	1·409	1·653
sec.-Nonyl ,, ...	0·637	—	0·846	1·000	—	—	—	1·651
sec.-Decyl ,, ...	0·641	—	0·848	1·000	—	—	—	1·649
sec.-Undecyl ,, ...	0·643	—	0·850	1·000	—	—	—	1·651
sec.-Dodecyl ,, ...	0·645	—	0·848	1·000	—	—	—	1·653
Average	0·641	—	0·847	1·000	—	—	—	1·651
Calculated	0·644	0·702	0·848	1·000	1·168	1·329	1·406	1·651

$\alpha_0 = 0{\cdot}2745$; $\lambda_0^2 = 0{\cdot}0237$.

Lowry and H. H. Abram[42] have devised a simple, practical method of testing if dispersion is simple or complex.

Anomalous Rotatory Dispersion.

In the neighbourhood of an *active* absorption band, rotatory dispersion is always anomalous. Near the absorption band, Drude's simple formula is not applicable. This is owing to the fact that in developing the formula certain terms, the effect of which is appreciable only in the neighbourhood of an absorption band, are neglected. It can, however, be deduced from the theory, if these terms are retained, that in the next neighbourhood of the absorption band the dispersion curve, after passing through a maximum, changes sign, and then passes through a second maximum of the opposite sign. Furthermore, the theory requires that between the two maxima the phenomenon of circular dichroism (the unequal absorption of the two circularly polarised rays into which the original plane vibration can be resolved) should be observable. The double maxima and the dichroism at an absorption band were first observed by A. Cotton[43] in 1896, and the phenomenon is known as Cotton's phenomenon. The phenomenon has recently been further investigated by Cotton[44] and G. Bruhat[45] with *l*-bornyl diphenylthiourethane, discovered by L. A. Tschugaev.[46]

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[42] *Trans. Faraday Soc.*, 1914, **10**, 103; *A.*, ii, 786.

[43] "Recherches sur l'absorption et la dispersion de la lumière par les milieux doués du pouvoir rotatoire." *Thèse*, Paris, 1896.

[44] *Compt. rend.*, 1911, **153**, 245.

[45] *Ibid.*, 248; *A.*, 1911, ii, 829.

[46] *Ber.*, 1909, **42**, 2244; *A.*, 1909, ii, 631. *Trans. Faraday Soc.*, 1914, **10**, 71.

Cotton's phenomenon can, according to the theory, become very complicated, and several of the deductions from the theory concerning it still await verification.

Tschugaev has shown that a very close parallelism holds between the absorption and the dispersion produced by active coloured substances in different solvents, the absorption and the dispersion curves being always displaced in the same direction in passing from one solvent (toluene) to another (acetone). Yet it is by no means always the case that there is a complete parallelism between the presence of an absorption band and the appearance of anomalous dispersion in the visible spectrum,[47] and, indeed, the electronic theory of dispersion would not lead us to expect that such would be the case. Drude assumes that the dispersion electrons are constrained by the asymmetric structure of the ether in which they are situated to move backwards and forwards in short helices, whereby a selective absorption of one of the circularly polarised components of the plane polarised light is occasioned. This selective absorption clearly depends on two factors, namely, the rate at which the electron absorbs energy from the ether, or its absorptive power, and the enantiomorphism of the space in which it is situated. Therefore the power of an absorption band to give rise to optical rotatory dispersion is dependent on the situation in the molecule of the electron to which the absorption band is due. In other words, the value of a constant k in Drude's formula, $a = \Sigma \frac{k_n}{\lambda^2 - \lambda_n{}^2}$, depends on the number of electrons with natural period λ_n in unit space, the position of each of these in the enantiomorphous molecule, and the absorptive power of each. The sign of k is positive or negative, according as the helix in which the electron corresponding with k moves is right-handed or left-handed.

Anomalous dispersion can occur in a region of the spectrum remote from an absorption band. In this case, Drude's approximation formula can be used to analyse the character of the dispersion. It is obvious that for anomalous dispersion of this class to occur, the formula expressing it must contain at least two terms. The examination of the equation:

$$a = \frac{k_1}{\lambda^2 - \lambda_1{}^2} + \frac{k_2}{\lambda^2 - \lambda_2{}^2}$$

will disclose the fact that a is a maximum at the wave-length λ, that is, anomalous dispersion can occur if

$$\frac{k_1}{k_2} = -\frac{(\lambda^2 - \lambda_1{}^2)^2}{(\lambda^2 - \lambda_2{}^2)^2},$$

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[47] L. A. Tschugaev and A. Ogorodnikov, *Zeitsch. physikal. Chem.*, 1913, **85**, 481; *A.*, ii, 8.

a condition which can be fulfilled when k_1 and k_2 are of opposite sign, and $k_2 > k_1$ when $\lambda_1 > \lambda_2$.

Owing to the difficulty of obtaining data of sufficient accuracy to determine the four arbitary constants in the above equation, the attempt to interpret anomalous rotatory dispersion of the class under consideration in the light of the electronic theory has been only quite recently undertaken. Lowry and Dickson[48] have measured the rotations of dextrorotatory ethyl tartrate over the visible spectrum and in the ultra-violet, employing a column of the liquid 6 dcm. long, and have shown that the readings can be represented with sufficient accuracy by the formula:

$$a = \frac{132{\cdot}78}{\lambda^2 - 0{\cdot}026} - \frac{103{\cdot}05}{\lambda^2 - 0{\cdot}061}.$$

In accordance with the requirements of the formula, a maximum value of the rotation was observed at the wave-length 5780, and a zero value in the ultra-violet at 4250, the lævorotation having been traced as far as $-83°$.

The view is held by some authorities that the bands to which the anomalous dispersion of ethyl tartrate is due, belong to different desmotropic forms of the ester; that, in fact, the anomalous dispersion is caused by the presence of two substances differing in rotatory dispersion as well as in the sign of their rotation.

The influence of temperature and of solution on the rotatory dispersive power of substances has for many years claimed the attention of a large number of investigators, amongst whom may be mentioned Frankland, Winther, and in particular T. S. Patterson. Until quite recently, the investigation of this problem has been restricted to monochromatic light. Early in 1913, Patterson summarised the position of the subject.[49]

Twenty years ago, it was thought that the temperature-rotation curve of a substance like ethyl tartrate, for example, became asymptotic to the axis of temperature. However, Frankland and Wharton observed that a minimum rotation could be observed with the substance ethyl dibenzoyltartrate. Later, C. Winther,[50] by the examination of the temperature-rotation curves of a number of substances, concluded that at a definite temperature the rotation becomes a maximum in the case of each of the substances. Patterson[51] then demonstrated that the maximum exists. Dilution of the active substance with an indifferent substance has the effect of moving the maximum through a range of temperature. In nitrobenzene, for instance, the maximum rotation of ethyl tartrate, which occurs at a temperature of about 175°, moves rapidly towards a lower value as the solution becomes more dilute, the rotation, at the same time, becoming gradually greater. Other solvents have the opposite effect; they cause the maximum to move towards a higher temperature. It appears to be possible to explain the above results on the assumption that the constants k in Drude's formula vary continuously on dilution with an indifferent solvent or on raising the temperature, whilst the absorption bands remain fixed.[52]

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[48] *P.*, 1913, **29**, 185; *Trans. Faraday Soc.*, 1914, **10**, 96; *A.*, ii, 786.

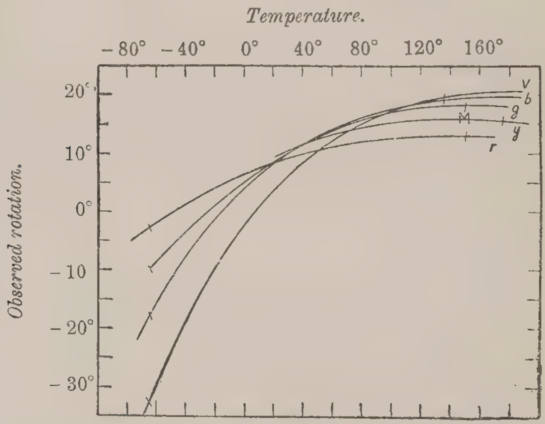
[49] *T.*, 1913, **103**, 151.

[50] *Zeitsch. physikal. Chem.*, 1902, **41**, 176; *A.*, 1902, ii, 589.

[51] *T.*, 1908, **93**, 1843.

Of still greater interest is the relation between the temperature-rotation curves of light of different refrangibility. A family of such curves was plotted by P. Walden,[53] the substances examined being ethyl and propyl tartrates. The diagram for ethyl

Ethyl tartrate. Rotation dispersion.



tartrate, taken from Patterson's paper,[54] is given above. It will be observed that the curves form an envelope. If the dispersion of the ester can be represented by Lowry's two-term formula, the envelope should lie entirely on one side of the axis of zero rotation and start very near this axis in the infra-red.

Winther has published similar temperature-rotation curves for solutions of tartaric acid in water and in alcohol. The length of the envelope in the visible spectrum of such a series of curves is generally short. The region of the diagram which includes the envelope is designated by R. H. Pickard and J. Kenyon[55] the region of anomalous dispersion.

[52] Lowry and Dickson, *loc. cit.*

[53] *Ber.*, 1905, **38**, 366; *A.*, 1905, ii, 130.

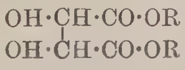
[54] *T.*, 1913, **103**, 165.

[55] *Ibid.*, 1914, **105**, 830.

H. E. Armstrong and E. E. Walker[56] have proposed a convenient diagrammatic method of representing the dispersive power of any one substance under varying conditions. On this diagram, the length of the ordinate represents the specific rotation. "To construct the diagram characteristic of a substance, a reference line is drawn with a slope of unity, and on this are plotted the various specific rotations of light of any one of the refrangibilities observed. The points for other refrangibilities are then plotted on the ordinates passing through the points previously located on the reference line. The observations may be those made either at different temperatures or in different solvents or at different concentrations."

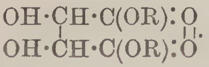
When diagrams for methyl tartrate, ethyl tartrate, and 2-nitrotoluene-4-sulphonyltetrahydroquinaldine were constructed according to these directions, the points corresponding with light of one refrangibility were found to lie always on smooth curves (nearly straight lines), although the rotations were made from observations on the substance under the most diverse conditions, and although the curves crossed one another in such a manner as to enclose an envelope. To obtain the diagram for ethyl tartrate, data published by C. Winther[57] were used. These included determinations of the specific rotation of the ester in the pure state and in the solvents, formamide, water, methyl alcohol, ethyl alcohol, chloroform, and ethylene dibromide.

The widest interpretation that can be assigned to the generalisation that the specific rotation of a substance is given by a single family of curves is that each of the constants in Drude's formula is a function of a single parameter. This single parameter would, according to the views of Patterson, be the pressure on the molecule. The generalisation that the specific rotation of a substance is in general a function of the wave-length and a single independent variable, is the outcome of the work of Patterson and Winther. Armstrong and Walker have suggested that the esters of tartaric acid probably consist of mixtures of desmotropic forms. Two possible forms are:



$$\begin{array}{l}\mathrm{OH\cdot CH\cdot CO\cdot OR}\\ \quad\;\; |\\ \mathrm{OH\cdot CH\cdot CO\cdot OR}\end{array}$$

and



$$\begin{array}{l}\mathrm{OH\cdot CH\cdot C(OR){:}O}\\ \quad\;\; | \qquad\qquad\quad\; |\\ \mathrm{OH\cdot CH\cdot C(OR){:}O}\end{array}.$$

They assume that the dispersion of each of these forms is normal, but that one is dextrorotatory and the other lævorotatory. A mixture of the two could then exhibit anomalous dispersion.

If the dispersion formula of the one form is $\alpha_1 = \frac{k_1}{\lambda^2 - \lambda_1^2}$, that of the other $\alpha_2 = \frac{k_2}{\lambda^2 - \lambda_2{}^2}$, and n is the ratio in which the two forms are present in the mixture, then the dispersion formula of the mixture is

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[56] *Proc. Roy. Soc.*, 1913, [*A*], **88**, 388; *A.*, 1913, ii, 543.

[57] *Zeitsch. physikal. Chem.*, 1907, **60**, 582; *A.*, 1907, ii, 831.

$$\alpha = \frac{nk_1}{\lambda^2 - \lambda_1{}^2} + \frac{(1-n)k_2}{\lambda^2 - \lambda_2{}^2}$$

and the mixture would exhibit anomalous dispersion if k_1 and k_2 were of opposite sign, and $nk_1 < (1-n)k_2$ when $\lambda_1 > \lambda_2$.

Now it is well known that in the case of a substance which exhibits normal dispersion, the rotation varies but little and the dispersion scarcely at all; so that, if, as Armstrong maintains, the desmotropes of tartaric esters are "normal" substances, the quantities k_1, k_2, λ_1, λ_2 can be taken as constant, and the single parameter in the formula for the specific rotation of the ester is n, the ratio of the two desmotropic forms.

G. Bruhat[58] has shown that the specific rotation curves (the curves obtained by plotting wave-length against specific rotatory power) of fused and superfused tartaric acid at different temperatures are the same family of curves as the specific rotation curves of solutions of the acid of different concentrations in water and in mixtures of alcohol and water. This is another example of the law that the specific rotation is a function of the wave-length and a *single variable*, and Bruhat's explanation of the fact is the same as that advanced by Armstrong and Walker, namely, that the acid is a desmotropic mixture.

It has recently been shown by Tschugaev[59] that anomalous dispersion may be produced by the superposition of the partial rotations produced by two asymmetric complexes within the molecule of an active substance, the necessary condition being, of course, that these partial rotations should be of opposite sign and should possess different dispersion ratios. The truth of the proposition was incontestably demonstrated by the application of van't Hoff's principle of optical superposition[60] to rotatory dispersion measurements made with *l*-menthyl *d*-β-camphorsulphonate and *l*-menthyl *l*-β-camphorsulphonate.

That the anomalous dispersions of *l*-menthyl *d*-β-camphorsulphonate and ethyl tartrate are separately due to absorption bands in a single substance, on the one hand, and to absorption by a mixture of desmotropic forms, on the other, can be shown to be probable in the following way. The conditions that maxima of rotation may occur at a wave-length λ are given by:

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[58] *Trans. Faraday Soc.*, 1914, **10**, 84; *A.*, ii, 787.

[59] *Ber.*, 1911, **44**, 2023; *A.*, 1911, ii, 787.

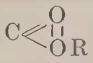
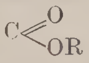
[60] The departures from van't Hoff's principle observed in certain cases by Patterson (*T.*, 1905, **87**, 40; 1906, **89**, 1884; 1907, **91**, 705) are always small, and never of sufficient magnitude to invalidate Tschugaev's conclusions.

$$\frac{nk_1}{(1-n)k_2} = \frac{(\lambda^2-\lambda_1^2)^2}{(\lambda^2-\lambda_2^2)^2}$$

in the case of the tartaric ester, and

$$\frac{k_1}{k_2} = \frac{(\lambda^2-\lambda_1^2)^2}{(\lambda^2-\lambda_2^2)}$$

in the case of Tschugaev's ester. The quantity $\frac{nk_1}{(1-n)k_2}$ will have very different values in different solvents, whilst $\frac{k_1}{k_2}$ will be approximately constant. Therefore, in the case of the tartaric ester, the maximum rotation should occur at very different wave-lengths in different solvents, but in the case of Tschugaev's ester, the maximum rotation should always be at approximately the same position in the spectrum.

In agreement with this conclusion, the maximum rotation of Tschugaev's ester in solution in toluene, acetone, and chloroform is approximately at the wave-lengths 527, 486, and 472 respectively, whereas in the case of ethyl tartrate the wave-length of maximum specific rotation varies so enormously for solutions in different solvents that it is only for a limited number of solutions that it corresponds with light in the visible spectrum. R. H. Pickard and J. Kenyon[61] have shown that the simpler esters, $CH_3{\cdot}CHR{\cdot}CO_2R^1$, all exhibit anomalous dispersion. Moreover, the dispersion is of the class which can be explained on the hypothesis of a mixture of isodynamic forms. The forms may be due to constitutional differences in the carboxyl group, capable of representation by  $\mathrm{C}{<}\begin{array}{l}\mathrm{O}\\ \,|\,|\\ \mathrm{OR}\end{array}$ and  $\mathrm{C}\begin{array}{l}{=}\mathrm{O}\\ {-}\mathrm{OR}\end{array}$.[62] The authors have made the interesting discovery that all the esters have the same characteristic diagram, from which it can be inferred that the corresponding isomerides of various members of the group of esters have the same or very closely related wave-length rotation formulæ. They point out that by plotting the characteristic diagram of an ester it is possible to discover if the active alcohol from which the ester was prepared has been completely resolved, incomplete resolutions being indicated by the characteristic diagram of the ester not fitting on the group diagram. They have also apparently solved the problem of determining in which of the two substituting reactions of a Walden inversion the change of configuration occurs. This is an achievement of first-rate importance. The following is the example cited by the authors: "Octan-β-ol with $[\alpha]_D^{20}$ +9·9°

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[61] *T.*, 1914, **105**, 830.

[62] Ida Smedley, *ibid.*, 1909, **95**, 231.

corresponds with β-bromo-octane with $[\alpha]_D^{20}$ −27·5°, which can be reconverted into the alcohol. Apparently, this lævorotatory bromide does not fit on the 'group' characteristic diagram for the *d*-octyl derivatives, but will do on a diagram which is the mirror image of the one illustrated, so permitting the inference that a change of configuration has taken place during the replacement of hydroxyl by bromine (by means of the action of hydrogen bromide)."

Although some valuable generalisations concerning the influence of constitution on the rotatory power of organic substances have been made from a study of the subject with sodium light, modern work clearly indicates that more rapid and certain progress will be gained in this important branch of the subject by the study of the compounds under more diverse conditions, employing monochromatic light of different wave-lengths covering the range of the spectrum. Amongst the most important achievements obtained with the use of sodium light may be mentioned:

(1) Tendency of the chain in homologous series to return upon itself at certain fixed points;[63]

(2) The effect of unsaturation;[64]

(3) The effect of distance from the centre of asymmetry;

(4) Superposition of the effect of several centres of asymmetry in the molecule, and

(5) The comparative influence of aromatic and fatty groups.[65]

Magnetic Rotatory Power and Wiedemann's Law.

Negative magnetic rotations are confined to a small range of metallic compounds, and therefore anomalous magnetic dispersion in a region of the spectrum remote from an absorption band is not to be expected in the case of organic compounds. This fact alone is sufficient to indicate that there cannot be a general simple relationship between magnetic and optical rotatory powers. However, more than half a century ago, G. Wiedemann, from experiments with turpentine, concluded that the ratio of the magnetic and the optical rotatory powers of one and the same substance is the same for light of all refrangibilities. E. Darmois[66] concludes from measurements of the optical and magnetic dispersion of compounds of the terpene series that "the law of proportionality is quite inexact, and that Wiedemann's result was the result of pure chance"; moreover, he concludes that, since normal magnetic dispersion can accompany anomalous optical dispersion, "Wiedemann's law has no longer any manner of significance." Lowry[67] assails Darmois' unqualified denial of Wiedemann's law. He finds that the law holds almost within the limits of experimental error for quartz, as may be seen from the following numbers:

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[63] P. F. Frankland and R. H. Pickard and J. Kenyon, *T.*

[64] T. P. Hilditch *T.*, and H. Rupe, *Annalen.*

[65] Rupe and Hilditch have contributed to the Faraday Society (*loc. cit.*) important summaries of past work on constitution and rotatory power.

[66] *Ann. Chim. Phys.*, 1911, [viii], **22**, 247, 495; *A.*, 1911, ii, 352.

	Li.	Na.	Hg.	Cd.	Cd.	Hg.
Wave-length	6708	5893	5461	5086	4800	4359
Dispersion ratios: magnetic	0·646	0·851	1·000	1·167	1·318	1·627
Dispersion ratios: optical	0·648	0·851	1·000	1·164	1·319	1·627

The fact that Wiedemann's law cannot hold for organic liquids is obvious from the circumstance that the magnetic rotatory dispersion of all organic liquids is normal, whereas the optical rotatory dispersion, more often than not, shows marked anomalies.[68] In tartaric acid, for example, the optical rotatory power is given by the formula $\alpha = \frac{k_0}{\lambda^2 - \lambda_0^2} + \frac{k_1}{\lambda^2 - \lambda_1^2}$ in which k_0 and k_1 have opposite signs, whereas the magnetic rotatory power is given by a one-term formula or, more probably, by a two-term formula, in which λ_0 and λ_1 have the same value as in the optical dispersion formula, whilst k_0 and k_1 have the same sign, but assume values different from those of the corresponding constants in the optical formula.

Lowry, Pickard, and Kenyon suggest that it is possible that Wiedemann's law will be found to be true for all optically active crystals in which the activity is caused solely by the arrangement of the molecules.

The Mechanism of Electrical Conduction.

C. A. Kraus[69] has continued his work on the solutions of metals in liquid ammonia. He has shown that it is highly probable that concentrated solutions of sodium in this solvent contain negative electrons, which partake in the process of conduction through the solutions. These solutions apparently bridge the gap between metallic and electrolytic conductors.

Determined efforts have again been made to disentangle the numerous factors which influence the conductivity of solutions, in order to prepare the way to determining the proportion of ions in such solutions, and to discovering the exact law of equilibrium between ions and the uncharged molecules from which they are derived. There is apparently a growing belief in the validity of the law of mass-action for solutions, of sufficient dilution, of all electrolytes, whether strong or weak.

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[67] *Phil. Trans.*, 1912, [*A*], **212**, 261.

[68] T. M. Lowry, R. H. Pickard and J. Kenyon, *T.*, 1914, **105**, 94.

[69] *J. Amer. Chem. Soc.*, 1914, **36**, 864; *A.*, ii, 520.

The difficulty of estimating the conductivity of highly diluted solutions arises from the uncertainty as to the right correction to be applied for the conductivity of the solvent. S. Arrhenius[70] discusses this correction. He shows that if the conductivity of the solvent is due to carbonic acid, the usual method of correction is theoretically right if the electrolyte is an acid stronger than acetic acid or a salt of a strong acid. If, however, the electrolyte is a salt of a weak acid, the correction to be applied is less than the conductivity of the solvent, and depends on $\frac{k}{c}$, where k is the ionisation-constant of the acid and c the concentration of the salt. With the aid of Kohlrausch and Maltby's conductivity measurements on sodium chloride and sodium nitrate, it is shown that at the highest degrees of dilution the conductivity data are in harmony with the law of mass-action. For both salts, the ionisation-coefficient $k = \frac{a^2}{(1-a)v}$ is equal to 0·024. Arrhenius expresses the view that at a sufficiently great dilution the ionisation of all electrolytes is in accord with the law of mass-action. The same assumption is implicitly made in the general formulæ which have recently been proposed to connect a, the ratio of the equivalent conductivity, Λ, to the equivalent conductivity at infinite dilution, Λ_0 with the concentration. Of these formulæ, that of Kraus and Bray was mentioned in last year's Reports. That advanced by J. Kendall, namely,[71]

$$\frac{a^2}{(1-a)v} = K + \frac{1-a}{a},$$

has been further tested by its author with the aid of conductivity data of concentrated solutions of weak acids.[72] He finds that the formula is not valid for such solutions, and he proposes a new dilution law for weak acids, which is expressed by the equation $\frac{a^2}{(1-a)v} c_s = K$, in which c_s is the concentration of the solvent in the solution. He claims to have shown that the ionisation-coefficient is influenced by two factors, namely, the total concentration, which causes the coefficient to diminish as the concentration is increased, and the ionic concentration, which has the opposite effect. That the latter factor is operative in the direction indicated has all along been the expressed opinion of most authorities.

With regard to the estimation of the concentration of the ion in the more concentrated solutions, one of the chief difficulties

[70] *Medd. K. Vet. Nobelinstitut*, 1913, **2**, No. 42 ; *A.*, ii, 93.

[71] *T.*, 1912, **101**, 1275.

[72] *Medd. K. Vet. Nobelinstitut*, 1913, **2**, No. 38 ; *A.*, ii, 93; and *J. Amer. Chem. Soc.*, 1914, **36**, 1069 ; *A.*, ii, 544.

has been to know what correction to apply for the viscosity of the solution. This question has been recently discussed very fully by C. A. Kraus,[73] who in his treatment of the subject has considered practically the whole existing experimental material. He comes to the important conclusion *that viscosity change affects the same ions differently when the viscosity change is brought about by different causes.* Thus, the mobilities of the ions of sodium chloride are proportional to the fluidity when the change in the latter is occasioned by a change of pressure, but the mobilities diminish less rapidly than the fluidity when the change is brought about by an alteration in concentration of the electrolyte. The author considers the correction which should be applied when the change in viscosity is brought about by: (*a*) the change in concentration of the dissolved electrolyte; (*b*) the dissolution of some non-conducting substance, such as sucrose, to the solution; (*c*) change of pressure; and (*d*) change of temperature. In investigating the effect of viscosity due to cause (*a*) on the mobility of the ions, it is essential to know the law of ionisation. This is assumed to be given by the equation $\frac{(c\alpha)^2}{c(1-\alpha)}=K+D(c\alpha)^m$, previously proposed by Kraus and W. C. Bray,[74] which has been shown to apply to conducting solutions in all solvents at dilutions below those for which it is necessary to apply a correction for viscosity. It is found that for a limited class of salts a value of α satisfying the above equation can be obtained from the expression $\frac{\Lambda\eta}{\Lambda_0\eta_0}$, in which Λ and Λ_0 are respectively the equivalent conductivity of the solution and the limiting equivalent conductivity, and η and η_0 are the viscosities of the pure solvent and the solution. Salts of this class are those of which both the ions have high mobilities, such as potassium iodide. Dilute solutions of these salts in water possess a viscosity less than that of pure water. In the case of salts of which one or both of the ionic mobilities are small, the expression $\frac{\Lambda\eta}{\Lambda_0\eta_0}$ gives a value of α which at the higher concentrations is greater than the values deduced from the equation of ionisation. In other words, the mobilities of the ions are proportional to the fluidity only when the change of fluidity is caused by the introduction of particles the dimensions of which are not greatly different from those of the molecules of the solvent.

The latter generalisation is supported by W. H. Green's[75] determinations of the equivalent conductivities at infinite dilution of solutions of salts in mixtures of water and non-electrolytes. For such solutions, Green has shown that $\Lambda_0\eta^p$ is a constant, the value of p being less than unity when the non-electrolyte is sucrose, but almost equal to unity when the non-electrolytes are substances of smaller molecular weight—glycerol and carbamide.

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[73] *J. Amer. Chem. Soc.*, 1914, **36**, 35; *A.*, ii, 90.
[74] *Ibid.*, 1913, **35**, 1315; *A.*, 1913, ii, 914.
[75] *T.*, 1908, **93**, 2049.

The inferences drawn by the author from the influence of temperature on the viscosity of water and on the limiting equivalent conductivity of solutions of salts in water are interesting. J. Johnston[76] has shown that the Λ_0 values of the different ions can be expressed as the simple exponential function, f^p, of the fluidity, f, of the pure solvent. The values of p for the larger and less mobile ions, such as the acetate ion, are almost unity, whilst those for the more rapidly moving ions are less than unity, the order of the ions, arranged according to increasing mobility, being, with one or two exceptions, identical with the order of decreasing values of p. Accordingly, as the temperature is raised, the mobilities of all the ions approach the same value, that is, all the ions tend to become of equal size. Now, as the mobilities of the larger ions (the acetate and the sodium ions, for example) increase at the same rate as the fluidity of water, it is unlikely that such ions alter much in size. It is more probable that the smaller ions grow and become more nearly equal in size to the larger ions as the temperature is raised. This increase in size can only be explained by an increasing tendency to become hydrated. According to Kraus, the size of an ion increases, and depends more on the charge and less on the intrinsic nature of the ion as the temperature is raised. The above conclusions as to the effect of temperature on the hydration of the ion ought to be capable of being verified by independent experimental evidence.

Very comprehensive investigations have been published on the conductivity and viscosity of solutions of various strengths of the chloride, bromide, iodide, and nitrate of rubidium in mixtures of acetone and water at temperatures ranging from 15° to 45°,[77] and on the fluidity and conductivity of sodium iodide and potassium iodide in mixtures of alcohol and water at temperatures ranging from 15° to 35°.[78]

Although it has been known for some years that every solvent has the power of ionising salts dissolved in it, it is still customary to speak of the solvents with low ionising power as non-ionising solvents. P. Walden[79] gives an exhaustive summary of the work in this subject, and also an account of the result of his own measurements on solutions of various tetra-alkylammonium salts in a number of different solvents. His results point to the conclusions that in general the Nernst-Thomson rule is obeyed, and that the molar-conductivity curves, although apparently exhibiting extreme dissimilarities, can be regarded as modifications of the same typical form.

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[76] *J. Amer. Chem. Soc.*, 1909, **31**, 1010; *A.*, 1909, ii, 854.

[77] P. B. Davis, H. Hughes, and H. C. Jones, *Zeitsch. physikal. Chem.*, 1913, **85**, 513; *A.*, ii, 20.

[78] E. P. Wightman, P. B. Davis, A. Holmes, and H. C. Jones, *J. Chim. phys.*, 1914, **12**, 385; *A.*, ii, 714.

The typical curve and its extreme modifications are satisfactorily explained by the theory of Kraus and Bray,[80] according to which the law of ionisation changes from the law of mass-action in dilute solutions to a law represented by Arrhenius' equation, $\frac{(c\alpha)^2}{c(1-\alpha)} = D(c\alpha)^m$, in concentrated solutions.

Another investigation which tends to confirm the validity of Kraus and Bray's ionisation formula is that of A. Sachanov and J. Prscheborovski.[81] From determinations of the molecular conductivity of salts in various solvents of low dielectric capacity, they find that the fall of molar conductivity on dilution is given by the equation $\Lambda_v v^n = \text{constant}$, and this is precisely the form to which Kraus and Bray's equation reduces by approximation at the concentrations investigated.

It is obvious that the law of equilibrium between the ionised and non-ionised parts of a salt in a concentrated solution of a salt differs more widely from the law of mass action as the value of m in Kraus and Bray's equation for the ionisation becomes greater. Furthermore, Kraus and Bray have shown that as the dielectric constant decreases the value of m increases. Accordingly, the departure from the law of mass-action observed in the ionisation of electrolytes is greater when the dielectric constant has a small value, that is, when the attraction between the ions due to their electrostatic charges is large. There exists, therefore, strong evidence for the view that the electrostatic forces between the ions determine in a large measure the degree of ionisation. If this view were correct, a salt should ionise to a greater extent in a solution of another ionisable salt than in the pure solvent, and this should be especially the case in weak dielectric solvents. A. Sachanov[82] has tested this deduction by carrying out a series of electro-conductivity measurements with mixtures of electrolytes in solvents of low dielectric constant. He finds that when the dielectric constant of the solvent is low, the determined specific conductivity of the mixture is always larger than that calculated from the single conductivity values—in some cases as much as six times as large. The increase in the conductivity is greater the smaller the dielectric constant of the solvent, and solutions of two salts with a common ion in these solvents also show an increased conductivity. Therefore, in solvents of small dielectric constants electrolytes exert a dissociating action on one another.

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[79] *Bull. Acad. Sci. St. Pétersbourg*, 1913, 907, 987 : *A.*, ii, 21, 91.

[80] *Loc. cit.*, see also S. Arrhenius, *T.*, 1914, **105**, 1414.

[81] *Zeitsch. Elektrochem.*, 1914, **20**, 39 ; *A.*, ii, 92.

[82] *Zeitsch. physikal. Chem.*, 1914, **87**, 441 ; *A.*, ii, 419.

It is well known that Arrhenius[83] discovered that the rate of inversion of sucrose by weak acids is greatly augmented by the addition of neutral salts, and that he attributed the effect to the enhancement of the ionisation of the acid by the presence of the salt. J. W. McBain and F. C. Coleman[84] have, however, shown that the effect observed by Arrhenius can be fully accounted for by the catalytic effect of the molecules of undissociated strong acid produced by the interaction of the hydrogen ions of the weak acid and the anions of the salt. It may therefore be concluded that the addition of a highly ionised salt to a weak acid in solution in water does not appreciably affect the ionisation-constant of the latter. It should be here mentioned that G. S. Walpole's[85] accurate measurements of the hydrogen potentials of mixtures of acetic acid and sodium acetate tend, on the whole, to confirm the conclusion of McBain and Coleman.

The anomalous behaviour of strong electrolytes in aqueous solution cannot be accounted for entirely by the direct effect of the electrostatic attraction of the ions. The immediate result of the attraction would be the reduction of the activity of the ions, and this should cause the determined lowering of the freezing point to be less than that calculated from the degree of ionisation (as estimated by the conductivity method), whereas, in point of fact, the lowering of the freezing point is in most cases a little above the calculated value.

Moreover, the product of the concentration of the ions of a saturated solution of a sparingly soluble salt, in the presence of a salt with a common ion, is much more nearly constant than the concentration of the undissociated portion of the salt, and this proves that the activity of the ions decreases much less than the activity of the undissociated portion of the salt increases with increasing concentration.[86]

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[83] *Zeitsch. physikal. Chem.*, 1899, **31**, 197 ; *A.*, 1900, ii, 201.

[84] *T.*, 1914, **105**, 1517.

[85] *Ibid.*, 2501.

[86] A. A. Noyes, C. R. Boggs, F. S. Farrel, and M. A. Stewart, *J. Amer. Chem. Soc.*, 1911, **33**, 1650 ; *A.*, 1911, ii, 1074 ; A. A. Noyes and W. C. Bray, *J. Amer. Chem. Soc.*, 1911, **33**, 1643 ; *A.*, 1911, ii, 1074 ; A. A. Noyes and K. G. Falk, *J. Amer. Chem. Soc.*, 1910, **32**, 1026 ; 1912, **34**, 485 ; *A.*, 1910, ii, 929 ; 1912, ii, 527 ; J. Walker, *Brit. Ass. Reports*, 1911, **81**, 349.

Conductivity of Molten and Vaporised Salts.

Three important papers have appeared during the year, namely, one on the conductivity of the vapours of salts[87] and two on the conductivity of fused salts.[88]

Ionic Equilibria and Electrical Potential Across Semi-permeable Membranes.

F. G. Donnan, in collaboration with G. M. Green[89] and A. J. Allmand,[90] has continued the investigations on his theory as to the conditions of ionic equilibrium in the neighbourhood of a semi-permeable membrane.

If two solutions of a salt KA^1 of ionic concentrations C_1 and C_2 are separated by a semi-permeable membrane which freely permits the passage of the cation, but intercepts the anion, the difference of potential between the two sides of the semi-permeable membrane is given by the equation

$$\pi_2-\pi_1=\frac{Rt}{nF}\log\frac{C_1}{C_2},$$

if it is assumed that the osmotic pressure of the ions is given by the laws of ideal solutions.

The membrane was composed of copper ferrocyanide deposited in parchment, and the solute was potassium ferrocyanide. Both solutions were coupled with calomel electrodes, as shown below,

$$\text{Cal.}\ \overset{e_1}{\overset{\frown}{|}}\ \underset{(1)}{\mathrm{K_4Fe(CN)_6}}\ \overset{E_m}{\overset{\frown}{\|}}\ \underset{(2)}{\mathrm{K_4Fe(CN)_6}}\ \overset{e_2}{\overset{\frown}{|}}\ \text{Cal},$$

and the *E.M.F.* of the cell thus formed was determined. A similar cell without a separating membrane was then constructed, and its *E.M.F.* determined. If Δe denotes the measured difference of *E.M.F.* of the two cells and E_d the "diffusion potential" of the two potassium ferrocyanide solutions, E_m is given by the equation $E_m=\Delta e+E_d$. E_d was calculated from the usual formula.

The discrepancies between the values of E_m found experimentally and those calculated from the formula were not inconsiderable. There was some indication that these could be ascribed to uncertainty in the calculation of E_d.

The following deduction from the general theory of solutions has also been tested experimentally. If both ions of a salt can freely move from one position to another in a solution, the product of the concentrations of both ions will be the same in both positions when equilibrium is established if the laws of ideal solution hold, and if the variation in concentration of both of the ions is solely due to a difference in electrical potential. The theorem was tested by allowing potassium chloride to come to equilibrium on both sides of a semi-permeable membrane of copper ferrocyanide, the differences of potential between the two sides of the membrane being established by the addition of potassium ferrocyanide to the solution on one side only. The ionic products, $[\mathrm{K}^{\cdot}][\mathrm{Cl}']$, on both sides of the solution were found to be nearly equal when the difference between the total ionic concentration on the two sides was small, but when this condition was not fulfilled, considerable differences in the values of the two products were observed. The authors show that the discrepancies are largely due to the departure of strong electrolytes from the laws of ideal solutions.

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[87] S. J. Kalandyk, *Proc. Roy. Soc.*, 1914, [*A*], **90**, 634; *A.*, ii, 763.

[88] P. Walden, *Bull. Acad. Sci. St. Pétersbourg*, 1914, 405; *A.*, ii, 330; and C. Tubandt and E. Lorenz, *Zeitsch. physikal. Chem.*, 1914, **87**, 513; *A.*, ii, 516.

[89] *Proc. Roy. Soc.*, 1914, [*A*], **90**, 450; *A.*, ii, 705.

[90] *T.*, 1914, **105**, 1941.

The latter investigation demonstrates almost conclusively that the product of the ionic concentrations of the diffusible salt is greater on that side of the membrane on which the total ionic concentration is greater, and that a rise in the value of the product of the ionic concentrations is accompanied by a proportionately greater fall in the concentration of the non-ionised portion of the salt. This result is in complete conformity with the conclusions drawn from experiments on the solubility of sparingly soluble salts in solutions of salts containing a common ion, and, taken in conjunction with the determinations of the freezing points of dilute solutions of salts and the law of isohydric solutions, it indicates that the activity of an ion of a salt becomes less, and that of the undissociated molecule greater, as the total ionic concentration increases, the rise of the latter and the fall of the former being such that the total osmotic pressure is almost the same as that calculated from the total number of molecules (salt molecules and ions) present in unit volume of the solution on the assumption that the laws of ideal solutions hold.

Determination of the Electric Potential of the Solution of a Salt in Water or Alcohol.

It is usually assumed that, if the potential of a rapidly forming surface of mercury in a solution of a salt is the same as the potential of mercury at rest in the same solution, the potential of the mercury is the same as that of the salt solution. Some results[91] obtained with the dropping electrode have just been published which appear to show that this fundamental assumption is

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[99] E. Newbery, *T.*, 1914, **105**, 2553.

not even approximately true. Solutions satisfying the experimental requirement, that the difference of potential between the dropping and still mercury should be zero, were prepared by adding alkali sulphide and alkali cyanide to solutions of potassium or sodium chloride. When these solutions were employed to determine, in the usual way, the absolute potential of the calomel electrode, the results obtained depended upon whether alkali cyanide or alkali sulphide had been used to prepare the solutions. The discrepancies were much too large to be accounted for by boundary diffusion potentials.

Catalysis in Chemical Actions in Gases.

The publication of the work of Dixon and Crofts[92] on the firing of gases by adiabatic compression has clearly brought to light a new phenomenon, namely, the surprising effect of an excess of oxygen in promoting the combustion of electrolytic gas. The authors have determined the ignition-temperature of electrolytic gas and of mixtures of electrolytic gas with varying proportions of oxygen, hydrogen, and nitrogen by determining the minimum compression required to bring about combustion. The ignition-temperature of a mixture of hydrogen and oxygen in the proportion in which they combine to form water was 526—527°. The addition of nitrogen or hydrogen to the electrolytic gas raised the ignition-temperature. The effect of oxygen was the opposite of that observed with nitrogen or hydrogen—the addition of oxygen resulted in the lowering of the ignition-temperatures. There was a continuous fall in the ignition-point as oxygen was added until its volume was eight times that of the hydrogen. The phenomenon is not easy to explain. It is not likely that the striking contrast in the specific effects of nitrogen and hydrogen on the one hand, and of oxygen on the other, can be accounted for by the greater total radiating and conducting powers of the former gases. It is suggested by the authors that possibly the activity of oxygen at higher concentrations might be explained if oxygen formed some active polymeride under these conditions, or if the concentration of the oxygen brought about ionisation of the hydrogen molecules.

Mallard and Le Chatelier, and also Falk, stated that the addition of oxygen to electrolytic gas lowers the temperature of ignition. Their results, however, can scarcely be considered as having established the fact, inasmuch as their methods of experimenting were vitiated by grave sources of error, as shown by the discrepancies in their results and by the more complete knowledge of the correct conditions of experimenting gained from the investigations of Dixon, Coward, Bradshaw and Crofts. D. L. CHAPMAN.

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[92] H. B. Dixon and J. M. Crofts, *T.*, 1914, **105**, 2036.

INORGANIC CHEMISTRY.

During the year, a very large number of papers have been published which come within the purview of this Report. It is impossible to do more than refer to a very few of these, and it is with some regret that so many interesting investigations are of necessity omitted. At the same time, there have appeared papers of outstanding interest and importance—papers which seem likely to mark this year as above other years.

There is little doubt that the general trend of inorganic chemistry is on philosophic rather than purely preparative lines. Less interest must surely be found in the reading of the characterisation of new compounds, however novel these may be, than in the reading of pioneer work which marches steadily on into the unknown, bearing down old conventions where such oppose it, confident in its sense of conscious merit, and safeguarded by its sense of true proportion. Sure of its inherent accuracy and fully aware of its revolutionary influence on the treasured tenets of the chemistry of yesterday, such work must rivet the attention of all. When on the one side he is confronted with the disintegration of elements under electric stresses, and on the other he learns that the atomic weight of certain elements can vary by as much as 1 per cent., according to the parentage of those elements, and when, again, he is told that the physical constants of metals as now known are worthless, because they are perpetually in a state of change from allotrope to allotrope, the chemist of to-day may be likened to his forefather of pre-Avogadro days. As did his forefathers of those days, so also does he now await that great generalisation which shall co-ordinate and link up all the threads to found a new philosophy. Radioactivity, enhanced line spectra, the intra-stellar elements, active nitrogen and oxygen, atomic disintegration, atomic-weight variation, each at the moment a watertight compartment of research, all will be unified and embodied in the new philosophy of the twentieth century. Then will a new chemistry in its greater meaning emerge as a phœnix from the glowing parental fires of the many chemistries of to-day.

Little apology is needed for the pages in this Report which have been devoted to those investigations which are leading to the inception of the new philosophy. It is impossible to pass by without special notice Collie's work on the disintegration of certain elements, the work of Soddy and Hyman, Richards and Lembert, and of others on the atomic weight of lead. As regards the latter work, a suggestion as to there being more than one inhabitant of each gap in the periodic table was put forward by Sir W. Crookes many years ago, before radioactive phenomena were known. Made as it was to explain certain facts then under discussion, this suggestion was forgotten, together with the facts. It was reserved for Soddy and Fajans independently to enunciate their hypothesis, basing it on sound argument. It is inherently startling in conception, and one is privileged to ask how many elements are likely to be concerned and how many atomic weights may be rendered insecure. One could have wished that by some yet unknown process of radioactive disintegration the formation of the rare earths could be explained. It would be far more satisfactory could one look upon these mysterious elements as the final products of change from elements which occupy legitimate positions in Mendeléev's table. They would then be considered as parasitical growths arising from elements formed, no doubt, by natural synthetic processes. Be that as it may, there is no doubt that the new work on the atomic weight of lead is thoroughly sound, and that it supports the hypothesis of Soddy and Fajans in a most remarkable way.

As regards the work of Collie, there now seems little doubt of its absolute validity. First put forward last year in a somewhat tentative fashion, the very definite results recently recorded by Collie, Patterson, and Masson bring conviction in their wake. This work is critically discussed in the Report, and nothing further need here be added.

The remainder of the Report follows the lines of those of previous years, but, as was stated above, some regret is felt that want of space compels the omission of much that is interesting.

Atomic Weights.

The year has been signalled by very remarkable work on the atomic weight of lead of radioactive origin. In last year's Report on radioactivity, Professor Soddy gave an account of the generalisation which, amongst other facts, involves the existence in some of the places in the periodic table of several elements, differing in atomic weight, but remarkably similar in other properties. It follows that all the radio-elements which are chemically identical in character should occupy the same position in the periodic table.

Such elements are termed isotopic. The unknown end-products of all the known disintegration series fall into the place occupied by lead. If these products are entirely stable, the lead from radioactive minerals should differ in atomic weight according to the amount of thorium or uranium in the mineral. The atomic weight of the thorium isotope should be 208·4, and that of the uranium isotope should be 206·0. The experimental results obtained in four different laboratories support this in a very remarkable way.

In the first case, the atomic weight of the lead in Ceylon thorite was determined.[1] An analysis of this mineral showed the presence of 61·95 per cent. of ThO_2, 0·85 per cent. of U_3O_8, and 0·39 per cent. of PbO. The very small quantities of lead suggest that it is all of radioactive origin, none being present as an original constituent. If that be so, then the atomic weight of the lead should be about 208·2, since 10 parts of it arise from thorium to 1 part from uranium.

The lead was extracted from a kilogram of the mineral, and after the most careful purification about 1·2 grams of lead chloride were obtained. The atomic weight of this lead was compared directly with that of the lead in a sample of the chloride prepared from the ordinary nitrate in the same way as was the mineral specimen. The two specimens were compared by titration with silver nitrate solution, the methods of weighing being those adopted by Baxter and Wilson in their work, on which the international value is mainly based. In one set of experiments the ratio of the atomic weight of the lead from thorite to that of ordinary lead was found to be 1·0049, whilst in a second set it was 1·0042. The atomic weight of the lead from thorite was therefore 208·5 and 208·3, respectively, in the two sets of determinations. The difference between this and the accepted value is far greater than the probable error of experiment unless unknown sources of error exist.

A still more striking result has been obtained in the Harvard laboratories,[2] for in this case lead of radioactive origin from several sources was used, and the values of the atomic weight were found to differ very considerably, according to the origin of the lead. It is not necessary here to enter into a description of the methods employed in the purification of the various samples of lead chloride or of the details of the analysis which evolved the determination of the ratio Pb : Ag. They were carried through with that accuracy with which the name of Harvard is associated. It may perhaps be stated that the determinations made with any one sample of lead chloride agreed exceedingly well amongst themselves. The result may be tabulated as follows, the values of the atomic weights of the lead from the various sources being given:

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[1] F. Soddy and H. Hyman, *T.*, 1914, **105**, 1402.

[2] T. W. Richards and M. E. Lembert, *J. Amer. Chem. Soc.*, 1914, **36**, 1329; *A.*, ii, 653.

Lead from N. Carolina uraninite	206·4
Lead from Joachimsthal pitchblende	206·57
Lead from Colorado carnotite	206·59
Lead from Ceylonese thorianite	206·82
Lead from English pitchblende	206·84
Common lead...	207·15

Without doubt, these results are exceedingly remarkable, and they undoubtedly support the generalisation as to isotopic elements. They are entirely contrary to experience, for very careful investigations at Harvard have failed to reveal any difference whatever in the atomic weights of copper, silver, iron, sodium, and chlorine obtained from the most varied sources possible.

Again a spectrographic investigation of the lead of radioactive origin showed no difference between it and ordinary lead. Soddy and Hyman, however, found that one line, $\lambda = 4760{\cdot}1$, is much weaker in the case of the "thorite" lead.

The above results have received further confirmation. In one case, the atomic weight of lead from pitchblende was found by Baxter's method to be 206·736 as a mean of nine determinations.[3] In the second case,[4] lead was obtained from various radioactive minerals, and the atomic weights were determined by the Stas method from the ratio $Pb : Pb(NO_3)_2$. The lead from uranium minerals gave an atomic weight between 206·36 and 206·65, whilst that from monazite gave 207·08, the value for ordinary lead from galena being taken as 207·01.

As regards the report of the International Committee, no change is recommended in the values given in the table published in 1913. The report draws attention to certain investigations of varying importance that have been carried out. Reference may be made to one or two of these, and certain papers since published.

The density of oxygen has been redetermined after the gas, obtained in the first place by heating pure potassium permanganate, had been carefully fractionated.[5] The mean value from fifteen determinations of the weight of a normal litre (0°, 760 mm., sea-level, and a latitude of 45°) is 1·42906 grams. In combination with the values obtained by Morley and by Rayleigh, the most probable value is 1·42905 grams.

Some further work on the atomic weight of tellurium has been carried out by the conversion of tellurium hydride, TeH_2, into tellurium dioxide, TeO_2.[6] The hydride was prepared from aluminium telluride, and also by the electrolysis of a 50 per cent. solution of phosphoric acid with a tellurium cathode and a platinum anode. The gas was frozen in liquid air, and then formed white crystals, melting at −57° and boiling at 0°. The results support the view that tellurium is not complex, and that the present atomic weight, 127·5, is the correct value.

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[3] O. Hönigschmid and (Mlle.) St. Horovitz, *Compt. rend.*, 1914, **158**, 1796; *A.*, ii, 655.

[4] M. Curie, *ibid.*, 1676; *A.*, ii, 563.

[5] A. F. O. Germann, *ibid.*, 1913, **157**, 926; *J. Chim. phys.*, 1914, **12**, 66; *A.*, ii, 47, 454.

The atomic weight of copper relatively to that of silver has been determined by an electrolytic method,[7] the weights of the two metals deposited by the same quantity of current being compared. The mean of ten values gives for the atomic weight of copper $63{\cdot}563 \pm 0{\cdot}003$ ($Ag = 107{\cdot}88$).

Two determinations have been made of the atomic weight of mercury. In the first, mercuric oxide was converted to mercury by heating with metallic iron,[8] and the mean of nine very close values gave the atomic weight as $200{\cdot}37 \pm 0{\cdot}025$. This value is considerably lower than the accepted value, and the authors considered that the discrepancy might be explained by the presence of a small quantity of a higher oxide, but that the result called for a further investigation of the atomic weight. This has been carried out recently by Easley and Brann's method of conversion of mercury into mercuric bromide.[9] The values obtained lay between 200·50 and 200·62, and as a mean of nine experiments the value of $200{\cdot}57 \pm 0{\cdot}008$ was deduced, a value which is in close agreement with that now accepted.

The density of neon after purification from helium has been redetermined by Leduc.[10] This was experimentally found to be 0·695, referred to air as unity, from which by his formula the author calculates the atomic weight to be 20·15.

Some criticism has appeared of Auer von Welsbach's work on ytterbium (aldebaranium) and lutecium (cassiopeium), for which he found the atomic weights of 173 and 175 respectively.[11] The earths of the ytterbium group, in the form of their nitrates, have been submitted to fractional crystallisation, the stages in the separation being followed by measuring the coefficients of magnetisation of each fraction.[12] After 4000 crystallisations, eight fractions were obtained with the same coefficient, which is accepted as proof of the existence of a definite substance. The metal of the nitrate corresponding with these eight fractions is called neoytterbium, and has an atomic weight of 173·54. The arc spectra of the first and the last of these eight fractions were observed, and they were identical except for a few rays in the one fraction due to thulium, and a few in the other due to lutecium.

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[6] L. M. Dennis and R. P. Anderson, *J. Amer. Chem. Soc.*, 1914, **36**, 882; *A.*, ii, 456.

[7] A. G. Shrimpton, *Proc. Physical Soc., London*, 1914, **26**, 292; *A.*, ii, 774.

[8] G. B. Taylor and G. A. Hulett, *J. Physical Chem.*, 1913, **17**, 755; *A.*, ii, 128.

[9] H. B. Baker and W. H. Watson, *T.*, 1914, **105**, 2530.

[10] A. Leduc, *Compt. rend.*, 1914, **158**, 864; *A.*, ii, 361.

[11] *Monatsh.*, 1913, **34**, 1713; *A.*, ii, 130.

[12] J. Blumenfeld and G. Urbain, *Compt. rend.*, 1914, **159**, 323, 401; *A.*, ii, 731, 694.

Allotropy.

Two new modifications of phosphorus have been discovered during the course of some experiments on the effect of high pressure on the melting point of ordinary white phosphorus.[13] The first of these is a new form of white phosphorus, which changes reversibly into the ordinary modification, and the second is a form obtained irreversibly from the ordinary form at high pressures and moderate temperatures, and is 15 per cent. more dense than Hittorff's metallic red phosphorus. The white modification was first produced by increasing the pressure on ordinary phosphorus to about 11,000 kilogram/cm.^{2} at 60°. The transition temperature is a linear function of the pressure, and lies between $-76·9°$ at a pressure of 1 kilogram/cm.^{2} and 64·4° at a pressure of 12,000 kilogram/cm.^{2} By crystallisation from carbon disulphide at low temperatures, the new modification was obtained in the form of microscopic crystals belonging to the hexagonal system.

The black modification is readily obtained by heating ordinary phosphorus to 200° under a pressure of 12,000 kilogram/cm.^{2} The density of this substance is very high, being about 2·69, as against 1·83 for ordinary white phosphorus and 2·34 for Hittorff's metallic crystallised red phosphorus. It is certainly a new form, and is characterised by not being spontaneously inflammable; it can with difficulty be ignited, and may be heated to about 400° in air without catching fire. It bears some resemblance to red phosphorus in that it is attacked by cold nitric acid, but not by sulphuric acid, and it is not dissolved by carbon disulphide. When heated in a closed tube it vaporises and condenses on the colder parts of the tube to a mixture of red and white phosphorus. It would seem, therefore, that the vapours of the black and the red forms are, at least in large part, identical. In contradistinction from the red and the white varieties, it is a fairly good conductor of electricity, the specific resistance being 0·711 ohm per cm. cube at 0°. The temperature-coefficient has a large negative value, and the relation between temperature and resistance is nearly linear between 0° and 75°. The specific heat was determined between 100° and 30°, and was found to be 0·170, a value which is considerably lower than those recorded for the other modifications. The vapour pressure was determined, and was also found to be lower than that of red phosphorus. The new form, therefore, appears to be more stable than the red variety.

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[13] P. W. Bridgman, *J. Amer. Chem. Soc.*, 1914, **36**, 1344; *A.*, ii, 647.

The investigations on the allotropy of the metals have considerably extended during the year, since copper, cadmium, and zinc have been added to the list of those which possess allotropic modifications.[14] The proofs of the existence of the different forms are based on dilatrometric observations, and as yet the pure allotropes do not seem to have been prepared. In the case of copper, the transition temperature is 71·7°, and in the case of cadmium the transition temperature is 64·9°. With both these metals, however, it has been found that the transition temperature depends upon the previous thermal history of the metal, and therefore it is concluded that more than two allotropic modifications exist. It follows that these metals normally are metastable mixtures of at least two allotropes, and that they are continually changing slowly into the stable modifications at the ordinary temperature. These observations are of considerable importance, for they show that the physical constants of these metals, and in all probability of many others, have no definite significance. It will be necessary to redetermine these, and study the physico-chemical properties by making use of the pure allotropic forms. Certain anomalous results on record are explained by this work, for example, Matthiessen and Bose's observation of the disintegration of cadmium wires heated at 80°, and also of changes in the electrical conductivity of copper wires after these had been heated for several days at 100°. It is probable that the stable form of zinc was obtained in an almost pure form by Kahlbaum, Roth, and Siedler.[15] Again, the specific heat-temperature curves for copper, zinc, lead, aluminium, and silver are not continuous, but change abruptly at one or more points. This agrees with the dilatrometric observations for some of these metals.

Further work has also been carried out on the new form of sulphur, S_π, the discovery of which was noted in last year's report.[16] A method has been worked out whereby the quantities of S_λ, S_μ, and S_π can be estimated in a given mixture of the three, and this has been applied to samples of sulphur which had been treated in various ways. The velocity of change, $S_\pi \longrightarrow S_\mu$, has been investigated, and it is found to be very great at first, but to fall rapidly to a very small value when the quantity of S_π present is small. The maximum amount of S_π which it has been possible to obtain by heating sulphur to various temperatures is about 6·5 per cent. after the sulphur has been heated to 180°.

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[14] E. Cohen and W. D. Helderman, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 628; 1914, **17**, 60; *A.*, ii, 205, 654; *ibid.*, 1913, **16**, 485; 1914, **17**, 54, 122; *A.*, ii, 52, 652; *ibid.*, 1913, **16**, 565; 1914, **17**, 59; *A.*, ii, 127, 652; *Zeitsch. physikal. Chem.*, 1914, **87**, 409, 419, 426; E. Cohen, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 632; 1914, **17**, 200; *A.*, ii, 202, 799; *Zeitsch. physikal. Chem.*, 1914, **87**, 431.

[15] *Zeitsch. anorg. Chem.*, 1902, **29**, 177; *A.*, 1902, ii, 259.

[16] A. H. W. Aten, *Zeitsch. physikal. Chem.*, 1913, **86**, 1; *A.*, ii, 121.

A study has also been made of the effect of the three catalysts sulphur dioxide, ammonia, and iodine, which are known to have great influence on the equilibrium $S_\lambda \rightleftarrows S_\mu$. Ammonia was found considerably to shift the equilibrium, with the result that the quantity of S_π was reduced to a very small value. The velocity of the change, $S_\pi \rightarrow S_\mu$, is about the same whether iodine is present or not. The bearing of the existence of S_π as a factor in the equilibrium on the properties of sulphur was considered, and it was shown that, in general, these are explained more satisfactorily than is possible on the lines of the old two-component system. Thus the change in viscosity with temperature, and the variation in crystallisation power with previous thermal treatment, are shown to be far better explained when the presence of S_π is taken into account.

Finally, analyses of solid sulphur, after treatment in various ways, are given, and it is shown that the quantities of S_μ present are always exceedingly small, and never greater than 0·1 per cent., and this only in sulphur that has been previously melted. Similarly, S_π is only to be found in sulphur that has previously been melted, and the maximum amount formed was 0·5 per cent. These results are very different from those given by Kruyt,[17] according to whom, sulphur which has been heated to 90° and 65° contains 3 and 2·4 per cent. of S_μ respectively. Kruyt, however, estimated the amount of S_μ by the change in melting point, and not by direct analytical methods.

Electric Discharge.

The work of Collie and Patterson and of Sir J. J. Thomson on the production of helium and neon in vacuum tubes during the passage of the electric discharge was dealt with at some length in last year's Report. During the year, several papers have been published upon this work, and there would seem to be little doubt that the evidence in favour of the actual production of these gases by the discharge has been materially strengthened. A very obvious criticism can be made of the detection of minute quantities of neon in the residuum after all the diatomic gases have been frozen out by means of charcoal cooled in liquid air, namely, that this gas arises from very small quantities of air which had leaked into the apparatus during the experiment. Such criticism might at first sight seem to be justified, because two independent observers have been unable to detect the production of either helium or neon when the possibility of leakage of air had absolutely been precluded.[18] [19] The fact that an exceedingly small quantity of air is necessary to give enough neon for spectroscopic detection was pointed out by Strutt, who found that 0·01 c.c. of air is amply sufficient. The failure of Strutt and of Merton to observe the formation of either helium or neon might therefore readily be interpreted as a somewhat effective criticism of the apparatus used in those experiments described in last year's report.

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[17] *Zeitsch. physikal. Chem.*, 1908, **64**, 513 ; *A.*, 1908, ii, 1028.

The essential improvement in the new apparatus described by Strutt and by Merton lies in the fact that the gas, after it has been subjected to the influence of the discharge, is not transferred to a second apparatus for analysis. The whole operation is carried out in one self-contained piece of apparatus, and in Merton's experiments, after the gas to be experimented with had once been introduced, it did not come into contact with any stopcocks. A singularly ingenious method of introducing hydrogen into the apparatus was devised by Merton in the shape of a small palladium tube sealed into a glass tube. The outer end of the palladium tube was hermetically closed, and by heating this tube with a Bunsen flame, small quantities of hydrogen diffused into the apparatus, which had previously been exhausted. There is no need to describe the actual experiments, since they gave negative results, despite the fact that they were similar in character to those previously carried out by Collie, Patterson, and Masson.

Quite apart, however, from the later results published by Collie, it does not seem possible to accept such a simple explanation as would seem to be suggested by Strutt and Merton's work. It must not be forgotten, in the first place, that if the neon found were due to an exceedingly small air-leak, the amount of argon would be enormously greater (700 times), and could not possibly escape detection. In the second place, the production of helium, which was so clearly noted in the early work, lies in a different category. Whilst neon might conceivably be due to air-leaks, the formation of helium in even greater amounts than the neon, which was definitely observed in several cases, can hardly be susceptible of the same explanation. The amount of helium present in the air is far less than that of neon, and therefore an air-leak would give the latter gas in considerable excess. With regard to the absence of argon, there is just the possibility that it might have been removed by the charcoal along with the diatomic gases. Be that how it may, there does not seem to be the faintest possibility that reasonable amounts of helium and little neon could be due to an undiscovered leak of air.

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[18] (Hon.) R. J. Strutt, *Proc. Roy. Soc.*, 1914, [*A*], **89**, 499; *A.*, ii, 201.

[19] T. R. Merton, *ibid.*, [*A*], **90**, 549; *A.*, ii, 726.

The problem gained considerable interest when Collie,[20] using Merton's own apparatus, obtained considerable quantities of helium and neon by the cathode-ray bombardment of powdered uranium metal in an atmosphere of hydrogen. Five grams of the uranium were finely powdered in a steel mortar, and then heated to redness in a vacuum for half an hour. The metal was then transferred to a small bulb, in which it could be bombarded by the cathode streams, and this tube was sealed on to the Merton apparatus. A small bulb containing charcoal, a hard glass tube containing copper and cupric oxide, and a small bulb containing phosphoric oxide, were also sealed to the apparatus. The whole was washed out several times with pure oxygen, and then exhausted until the discharge would not pass. The tube containing the uranium was then heated as strongly as possible, and the gases were pumped off and examined. Carbon gases and hydrogen were present, but only just sufficient helium and neon to be detected in the usual way. The tube was then again washed out with pure oxygen and re-exhausted to the utmost limit. A small quantity of hydrogen was admitted by heating the palladium tube for twenty to thirty seconds, so as to allow the discharge to pass. The bombardment of the uranium lasted for two hours, and during this time carbon gases and hydrogen were evolved. These were absorbed by cooling the charcoal with liquid air and by heating the cupric oxide. At the end, considerable quantities of helium and neon were found to be present, and the experiment was repeated several times with the same result. By slight variation in the treatment of the gases, nitrogen was found in small quantities, but this disappeared after sparking above the mercury in the containing vessel. Only very small traces of argon were noted, since it showed only the blue spectrum. During these experiments the gases did not come into contact with any stopcocks, and therefore the arguments against air-leaks as the origin of the monatomic gases appear absolutely sound, and the results would seem to discount the criticism that might have been based on Strutt's and Merton's work.

In describing these experiments, mention is made for the first time of a fact which may give the key to the divergent results obtained by the different observers, for it must be remembered that positive results were also obtained by Thomson, as well as by Collie and Patterson and by Masson, in 1913. In one or two experiments Collie found that by using a larger induction coil with a mercury break in place of the original 10-in. coil with a platinum break, no helium or neon was produced. On repetition of the experiments under exactly the same conditions, but with the old coil, it was found that the helium and neon were again produced to the same amounts as previously. The very small traces of nitrogen detected in the residual gases after the charcoal had been cooled is attributed by Collie to the presence of some nitride in the uranium. The presence of this trace of nitrogen and its spectroscopic detection is of some considerable importance. It is a well-known fact that very minute quantities of nitrogen can be detected by means of its spectrum, and, further, it is perfectly evident that only minute traces were present, since the gases had been for some time in contact with the charcoal cooled in liquid air. It may safely be deduced, therefore, that those positive results of helium and neon production when no nitrogen was observed (and these form by far the larger majority) could not in any way be due to air-leaks.

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[20] J. N. Collie, *Proc. Roy. Soc.*, 1914, [*A*], **90**, 554 ; *A.*, ii, 727.

In a recent paper the previous positive results are confirmed in a still more striking way, and also the question of possible air-leaks is very critically considered.[21] The precautions taken against such leaks are described in detail, and these leave no doubt that, whatever may be the origin of the production of helium and neon, it does not arise from faulty apparatus. In this paper the details of the various types of apparatus used by these authors in their separate and individual experiments are described more minutely than was the case in the previous papers. Very many different designs of discharge tubes were used, some with outer jackets and some without. In the case of the former, the jackets were either exhausted, filled with neon, or filled with water. Since these three alternatives made no apparent difference, it follows that the sole remaining possibility of external contamination is excluded, namely, the porosity of the glass of the discharge tube to helium and neon only during the discharge. This indeed savours of hypercriticism, but clearly even the most far-fetched hypothesis must be tested. As stated in last year's Report, both helium and neon were found in the outer jacket when the experiments were carried out with this vessel completely exhausted. This result, which has been confirmed, is perhaps the most extraordinary of all that have been recorded. It may be remarked here that numbers of control experiments were made, that is to say, the apparatus was left standing under exactly the same conditions as in actual experiments, but without any discharge being passed. In every such control no helium or neon was found.

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[21] J. N. Collie, H. S. Patterson, and I. Masson, *Proc. Roy. Soc.*, 1914, [*A*], **91**, 30; *A.*, ii, 847.

A great number of different types of experiments have now been made, including the discharge between various metallic electrodes, the bombardment of various metals, oxides, and salts, and the mercury arc lamp in silica tubes, with and without a water jacket. In all three types, both helium and neon were found in varying amounts. Many isolated experiments gave negative results, owing to reasons as yet unexplained. The most important part of the recent paper, at any rate to those who still maintain an attitude of destructive criticism, lies in a detailed discussion of the possible sources of error and the precautions that were taken against such errors. The question of atmospheric contamination must now be taken as being definitely decided, for the controls show that there is no leak in the apparatus, and the sole remaining possibility of the permeation of air through the walls of the discharge tube during the experiment is negatived by the absence of the nitrogen and argon spectra, and also by the fact that the use of an outer jacket, which entirely covers the discharge tube, makes no appreciable difference in the result.

In the writer's opinion, the strongest evidence yet advanced for the reality of the result is to be found in the fact that negative results are sometimes obtained, and that these have been traced in some cases to differences in the type of induction coil used. If, as now seems probable, the helium and neon are really disintegration products arising from the effect of the discharge, such negative results are bound to be obtained unless the discharge is tuned, as it were, to the tube used. In the earlier experiments the authors were fortunate enough in most cases to effect such tuning unconsciously, but when many and various types of tubes were tried the natural result happened. Success and want of success followed one another in an apparently inexplicable way, owing to want of tuning. One thing at least may be said, namely, that the negative results must surely rule out air-leaks as contributory causes unless such leaks exhibit a discontinuity in their behaviour, which wide experience shows to be entirely foreign to their nature.

It is a familiar fact to anyone who has carried out experiments on the phenomena taking place in vacuum tubes and electric discharge generally that the results obtained vary in a most perplexing way. The principal source of such variations seems to lie in the induction coil, the capacity of the discharge tubes, the nature of the discharge, etc. Such results afford keen disappointment to the experimenter when first met with, but they fall into line at once when their origin is explained. In the present work, their very existence and their explanation, at any rate in many cases, by the variation in electrical conditions do more to establish the validity of the positive results than destructive criticism can ever be relied upon to effect.

As regards the origin of these gases, it was stated above that there can be little doubt but that they rise from atomic disintegration under the influence of the discharge. Sir J. J. Thomson, as was detailed in last year's Report, favoured the view that the helium obtained had previously been occluded in the electrodes used or the substance bombarded. Against this view certain rigid tests must be recorded. In the first place, the positive results obtained with electrodeless discharge tubes prove that metallic electrodes are not necessarily the source, and, further, the production of helium and neon in the arc between mercury surfaces is against such a view, seeing that neither gas was obtained on boiling the mercury in a vacuum. Again, Collie, Patterson, and Masson did not experience the steady fall in the amounts of helium and neon obtained when the same tube was used several times in succession, as was noticed by Thomson. Further, the following tests were applied in connexion with certain sets of experiments. Positive results of helium and neon were, for example, obtained with a jacketed tube with aluminium electrodes and with hydrogen as the gas. All air-leaks were precluded by the jacket and by the fact that every control experiment gave no trace either of helium or neon. A quantity of the aluminium wire used in making the electrodes was melted in a vacuum, but gave off no trace of either gas, and the same was true of the glass out of which the tube had been made. A further portion of the aluminium wire was then dissolved in air-free potassium hydroxide solution. The hydrogen evolved was passed over heated cupric oxide, and the residue was examined in the same apparatus as used for the discharge experiments. Similarly, a large quantity of the glass was powdered and acted on by potassium fluoride and concentrated sulphuric acid in the absence of air. About 300—400 c.c. of silicon fluoride were collected, and frozen out by means of liquid air. In neither case was any helium or neon found in the residual gases. Similar negative results were obtained with old Roman and Chinese glasses. Some valuable support to this is obtained from some tests carried out by Sir J. J. Thomson, who found that aluminium salts gave the same quantity of helium on bombardment by cathode rays, whether they were made from ordinary aluminium metal or from the same metal which had originally had helium forced into it by being made the electrode of a helium tube. As Thomson says, this shows that solution can be trusted to eliminate adsorbed gas. It is unreasonable, therefore, in the extreme to suppose that if helium and neon were present as such in the materials used, they would not be set free on dissolution which is accompanied by gas evolution. Solution of aluminium in potassium hydroxide, for example, entails a far more thorough physical disintegration of the piece of metal than does the bombardment of its surface. The only tenable supposition is that any inert gases physically admixed must be set free; it is not possible to assume that anything more than a physical admixture in the case of inert gases pre-exists in aluminium or in glass. The proved absence of neon and helium from the resulting products of chemical reaction must prove, therefore, that they are absent altogether.

In conclusion, the case in favour of these gases being due to atomic disintegration seems overwhelmingly strong, and the writer feels that no apology is needed for so full an account of this work, which must rank as one of the most remarkable investigations of modern times.

Some noteworthy contributions have been made to the problem of active nitrogen, first discovered by Strutt, and further dealt with by him in papers described in the Reports for 1912 and 1913. It would seem that some doubt has been thrown on the mechanism of the production of the active nitrogen, that is to say, whether it is produced from absolutely pure nitrogen or whether a trace of oxygen is a necessary factor. It might at first be thought that it is a matter of secondary importance as to whether the oxygen is a contributory factor or not, seeing that the essential point has clearly been established, namely, that an active nitrogen does exist. It must not be forgotten, however, that the mechanism of the formation of this gas is not understood, nor has the reason of its abnormal reactivity ever been explained.

In last year's Report mention was made of some experiments which seem to prove that the presence of oxygen is a necessity for the activation of the nitrogen, but this statement was controverted by Strutt himself. The original experiments were again repeated, and, in spite of Strutt's contradiction, the authors maintained their position.[22] The greatest possible care was taken in the making of the apparatus and in the filling of it with absolutely pure nitrogen. No fat was used on the stopcocks, and all traces of mercury vapour were removed by means of gold-leaf cooled in liquid air. Several series of experiments were carried out, and in the last the nitrogen was prepared in the apparatus by heating barium azoimide to 170°. In each case no sign of the Strutt phenomenon was observed unless

[22] E. Tiede and E. Domcke, *Ber.*, 1913, **46**, 4095; *A.*, ii, 122.

small quantities of oxygen were mixed with the nitrogen. The oxygen was obtained by heating silver oxide contained in a small tube sealed to the apparatus.

A slightly different view of the phenomena has been put forward by Koenig and Elöd,[23] for they differentiate between the after-glow (Strutt's phenomenon) and the formation of the active nitrogen. The presence of the former is not necessary to prove the existence of the latter, a statement that is of some importance, since it was the after-glow which Tiede and Domcke used as criterion of the formation of the active nitrogen. The real test for the presence of active nitrogen lies in the reactions which can be carried out by its means. It was found, further, that active nitrogen can readily be prepared by passing the pure gas, at 15 mm. pressure, through a direct-current arc. The after-glow was then exceedingly well marked, and a number of new reactions of the activated nitrogen were observed. For example, ethylene and acetylene react vigorously, the after-glow disappears, and the region where the two gases meet is marked by a lilac flame showing the spectrum of cyanogen. Hydrogen cyanide is formed in a quantity corresponding with that found by Strutt. Pentane gives ammonia, amylene and hydrogen cyanide.

It was also found that when pure oxygen is passed through the arc, a weak, bluish-green after-glow is formed. If the glowing oxygen is mixed with glowing nitrogen from a second apparatus, both glows are immediately extinguished, and oxides of nitrogen are formed in quantity. If the arc is extinguished in either apparatus, the formation of the nitrogen oxides ceases at once. It is concluded from these experiments that an active form of oxygen is produced, differing from ozone and capable of existing only for a short time.

It may be pointed out that these results are in agreement with, and entirely confirm, those obtained by Lowry, and fully described in the Report for 1912. This seems to have escaped the notice of Koenig and Elöd, for they make no reference to the fact that the phenomenon had previously been discovered by Lowry.

In a further paper,[24] the results of Tiede and Domcke are adversely criticised. If mercury vapour is mixed with the nitrogen, the after-glow is not observed, although the active gas is still produced. The presence of alkali metal vapour has a similar effect, and thus the suggestion is made that Tiede and Domcke's results were due to the admixture of either mercury vapour or potassium or barium vapour (from the azoimides used to prepare the nitrogen).

Tiede and Domcke, however, carried out experiments with

[23] A. Koenig and E. Elöd, *Ber.*, 1914, **47**, 516 ; *A.*, ii, 264.

[24] *Ibid.*, 523 ; *A.*, ii, 266.

nitrogen from which all the oxygen had been removed by means of heated copper.[25] They state that with this nitrogen the Strutt phenomena are not obtained with iodine, sulphur, sodium, and thallium chloride, but the addition of the least trace of oxygen at once gives rise to the phenomena. In this work, the alkali metal vapours were certainly absent, and the precautions for removing mercury vapour would seem amply to be sufficient, so that Koenig and Elöd's criticism does not appear to be sound.

Baker and Strutt, on the other hand, found themselves quite unable to confirm these results, for on repeating the experiments they found the after-glow very pronounced, and also very decided evidence of the activity of the nitrogen.[26]

An interesting conclusion to the argument is arrived at in a joint paper by all four authors.[27] It is explained that the contradictory results are due very largely to differences in the apparatus used. Whereas with Tiede and Domcke's apparatus the brightness of the after-glow was increased by the addition of traces of oxygen, in Baker and Strutt's apparatus no appreciable diminution in the glow was observed when absolutely pure nitrogen was used. The conclusion is drawn that it is probable that the production of active nitrogen is favoured by traces of oxygen, although in a suitable apparatus the result can be obtained even with the purest nitrogen.

It is curious, however, that a real explanation of no active nitrogen being obtained by Tiede and Domcke is not given, unless it be attributed entirely to differences in the apparatus. If this is so, it is another and most interesting instance of the necessity of tuning the discharge to the type of tube used, such as was referred to above under Collie, Patterson, and Masson's work. At any rate, the criticism of Koenig and Elöd is effectively met by the facts published in the joint paper; this is pointed out in a final communication.[28]

Possibly this dependence on the relation between discharge and apparatus used is similar to that observed in the formation of ammonia from its elements under the influence of the silent discharge.[29] In this case, also, the amount of ammonia formed depends upon the dimensions of the apparatus and the density and the oscillation frequency of the current.

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[25] E. Tiede and E. Domcke, *Ber.*, 1914, **47**, 420; *A.*, ii, 196.

[26] H. B. Baker and R. J. Strutt, *ibid.*, 801, 1049; *A.*, ii, 357, 457.

[27] H. B. Baker, E. Tiede, R. J. Strutt, and E. Domcke, *ibid.*, 2283; *A.*, ii, 724.

[28] E. Tiede and E. Domcke, *ibid.*, 2284; *A.*, ii, 724.

[29] M. Le Blanc, *Ber. K. Sachs. Ges. Wiss., Math.-phys. Kl.*, 1914, **66**, 38; *A.*, ii, 809.

Group I.

In last year's Report reference was made to the preparation of pure anhydrous sodium monosulphide by the action of heat on the hydrosulphide. The action of sulphur on the hydrosulphide has now been investigated with the view of studying the polysulphides of sodium.[30] Approximately saturated solutions in alcohol of the hydrosulphide were heated on the water-bath with equivalent proportions of sulphur, and the product was either precipitated after cooling by the addition of ether or recovered by evaporation of the solution. Amounts of sulphur corresponding with the di-, tri-, tetra-, and penta-sulphides, as well as a large excess of sulphur, were used. The results are interesting, because the only pure solid compound obtainable by the above method was the tetrasulphide, Na_2S_4. With smaller quantities of sulphur, mixtures of the tetrasulphide and hydrosulphide were formed, and with greater quantities of sulphur the tetrasulphide, mixed with free sulphur, was obtained. On the other hand, there was definite evidence to show that higher polysulphides exist in the solution, and some indication was obtained that when a great excess of sulphur was used, small quantities of higher polysulphides were mixed with the tetrasulphide when the latter was separated in the solid phase. The solution in such cases would seem to contain equilibrium mixtures of the tetrasulphide and higher polysulphides, and confirmatory evidence of this was obtained by the determination of the hydrogen sulphide set free by the mutual action of weighed amounts of sulphur and sodium hydrosulphide in solution. The latter experiments certainly prove that the first action of the sulphur is to give the tetrasulphide, and if insufficient sulphur is used to convert the whole of the sodium hydrosulphide into the tetrasulphide, mixtures of the hydrosulphide and the tetrasulphide are obtained.

By the action of metallic sodium on a solution of the tetrasulphide in alcohol, the disulphide has also been prepared in a pure state. Sodium tetrasulphide, Na_2S_4, is a dark yellow, crystalline powder with an olive-green tinge. It is extremely hygroscopic, and dissolves in water to give a deep orange solution, which turns red on heating. The disulphide, Na_2S_2, is a bright yellow, microcrystalline powder, readily soluble in water to a deep yellow solution.

By heating known quantities of water and finely pulverised glasses of known constitution to high temperatures in a gold crucible contained in a special bomb, certain new crystalline alkali silicates have been prepared.[31] The temperature was measured by means

[30] A. Rule and J. S. Thomas, *T.*, 1914, **105**, 177.

[31] G. W. Morey, *J. Amer. Chem. Soc.*, 1914, **36**, 215; *A.*, ii, 202.

of a thermo-couple, and was accurate to ±5°. The following compounds were obtained: potassium hydrogen disilicate, $KHSi_2O_5$, orthorhombic crystals which do not lose water at 350°. The crystals are very little affected by water, and may be boiled for several hours at 100° without any appreciable decomposition. Potassium disilicate, $K_2Si_2O_5$, a compound which is hygroscopic and very readily acted on by water. Sodium disilicate, $Na_2Si_2O_5$, which resembles $KHSi_2O_5$ in optical properties; the crystals may be leached with water, but on prolonged contact they are decomposed. Sodium metasilicate, Na_2SiO_3, forms crystals which are very readily decomposed by water. This compound was previously known only in the form of somewhat indefinite hydrates.

Some interesting work on nitrites may be referred to in view of the bearing it has on the fixation of nitrogen.[32] This reference may conveniently be included here, in spite of the fact that much of it refers to the next group. The nitrites of the alkali and alkaline earth metals can be prepared in the pure state only by double decomposition of silver nitrite with the chlorides of these metals, and in this way two new nitrites, $LiNO_2,H_2O$ and $Ca(NO_2)_2,4H_2O$, have been obtained. The hydrated nitrites generally can be dehydrated in a vacuum over phosphoric oxide without decomposition. The solid nitrites and their saturated solutions are not oxidised by oxygen at atmospheric pressure. Oxidation takes place only in the presence of acid, when the free nitrous acid plays an important part in the reaction. The following double salts also were obtained:

$$Na_2Ag_2(NO_2)_4,H_2O,\ K_2Ag_2(NO_2)_4,H_2O, \text{ and } BaAg_2(NO_2)_4,H_2O.$$

In the action of heat on sodium nitrite, the following reactions take place in addition to the ordinary reactions:

$$NaNO_2 + NO_2 = NaNO_3 + NO, \quad 2NaNO_2 + NO_2 = 2NaNO_3 + N.$$

This explains the actions which occur when nitrogen peroxide acts on calcium oxide and on the alkali and alkaline earth carbonates. When nitrogen peroxide acts on calcium oxide, there is always a loss of nitrogen, whatever be the conditions of temperature, in accordance with the equation $2CaO + 5NO_2 = 2Ca(NO_3)_2 + N$, a fact that is of industrial importance.

An investigation has been made of the composition of the solutions in equilibrium with the four salts potassium chloride, sodium nitrate, sodium chloride, and potassium nitrate, which affords useful information as to the most economical production of "conversion" saltpetre.[33] If a solution containing sodium nitrate, potassium chloride, and water in the molar ratio 0·80 : 0·62 : 1·81 is evaporated at 100°, 0·42 mol. of sodium chloride is deposited. On cooling to 5°, the salts separate out in the proportion 0·575 mol. of potassium nitrate: 0·038 mol. of sodium chloride: 0·10 mol. of sodium nitrate. If, however, a suitable amount of water is added, the separation of solid sodium chloride and sodium nitrate can be avoided, and 0·563 mol. of potassium nitrate obtained in crystals, which represents a yield of 90·8 per cent.

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[32] M. Oswald, *Ann. Chim.*, 1914, [ix], **1**, 32; *A.*, ii, 197.

[33] W. Reinders, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 1065; *A.*, ii, 549.

Group II.

Metallic strontium has been obtained by the electrolysis of the binary mixture, strontium chloride–potassium chloride.[34] A eutectic point occurs with the mixture containing 15 per cent. of potassium chloride, and when the same method is used as in the case of calcium, sticks of strontium 10 cm. long and 1—2 cm. in diameter can be obtained. The mixture of chlorides melts at 628°, which is 220° below the melting point of strontium chloride. The current density must be 20—50 amperes per sq. cm. of cathode, and the efficiency is then 80 per cent. Metallic barium has also been obtained in a similar way.

The investigation of the phase systems of calcium nitrate has been extended to a study of the three-component system, calcium nitrate–lime–water.[35] The nature of the solid phases capable of existing in equilibrium with aqueous solutions of calcium nitrate containing lime was investigated at 25° and 100°. Only one definite basic nitrate, $Ca_2N_2O_7$, was found, which forms several hydrates, containing $\frac{1}{2}$, 1, 2, 3, and 4 molecules of water respectively. No series of solid solutions, CaO,xN_2O_5,yH_2O, were found such as postulated by Cameron and Robinson,[36] nor does the hydrate, $Ca_2N_2O_7,3\frac{1}{2}H_2O$, exist, as stated by these authors.

Some interesting work on calcium sulphate may be mentioned in connexion with its dehydration and commercial use as plaster of Paris.[37] When gypsum is heated at temperatures not above 210°, it becomes anhydrous, but the product is much less dense and more soluble than natural anhydrite. The conversion of the hemihydrate to the soluble anhydrite, which is the last stage in the dehydration process, is reversible, each process only requiring a few minutes at 110° in a dry and a humid atmosphere respectively. Since the hydration to the hemihydrate takes place so easily, this salt naturally forms the principal constituent of plaster of Paris. The best temperature for dehydration for commercial purposes depends upon the humidity of the air in the oven, thus explaining the variable results that have been obtained. The hemihydrate also absorbs water from the air at the ordinary temperature up to a total water-content of about 8 per cent. Microscopic and calorimetric observations confirm Le Chatelier's theory of the mechanism of the setting of plaster of Paris.

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[34] B. Neumann and E. Bergve, *Zeitsch. Elektrochem.*, 1914, **20**, 187; *A.*, ii, 365.

[35] H. Bassett, jun., and H. S. Taylor, *T.*, 1914, **105**, 1926.

[36] F. K. Cameron and W. O. Robinson, *J. Physical Chem.*, 1907, **11**, 273; *A.*, 1907, ii, 444.

[37] G. Gallo, *Gazzetta*, 1914, **44**, 1, 497; *A.*, ii, 561; C. Gaudefroy, *Compt. rend.*, 1914, **158**, 2006; **159**, 263; *A.*, ii, 650, 728.

Group III.

In the Reports for 1912 and 1913 reference was made to the isolation of the three hydrides of boron, B_2H_6, B_4H_{10}, and B_6H_{12}. The first two compounds dissolve in alkali hydroxide, giving solutions which do not smell of the hydrides, but are unstable, and tend to give up hydrogen.[38] Since the latter reaction takes place least easily with B_4H_{10}, this hydride was used in an investigation of the products formed when it is passed into aqueous alkali hydroxides. The first action takes place between one molecule of the hydride and four molecules of a monacid and two molecules of a diacid base, according to the equation

$$B_4H_{10} + 4KOH = 4KOBH_3 + H_2.$$

By treatment of potassium hydroxide dissolved in one and a-half times its weight in water with excess of B_4H_{10} at 0°, the solid hypoborate was obtained in the form of colourless, octahedral crystals. The formula $KOBH_3$ was proved by analysis. This substance is stable in the absence of moisture; it is deliquescent, and its solutions decompose slowly at room temperature in accordance with the equation

$$2KOBH_3 + 2H_2O = 2KBO_2 + 5H_2.$$

This reaction is brought about immediately by the addition of acid. The aqueous solution of the hypoborate is a very powerful reducing agent. With copper salts it gives a precipitate of copper hydride, and with nickel salts a black, insoluble nickel boride, NiB_2. This compound is non-magnetic, but on heating to 500° it becomes magnetic, at the same time sintering to a grey, metallic form.

When the compound $KOBH_3$ is heated at 500°, metallic potassium, hydrogen, and water are expelled, and the reaction is probably expressed by the equation

$$5KOBH_3 = K_3B_5O_3 + 2K + 2H_2O + 11H.$$

The residue, $K_3B_5O_3$, is somewhat hygroscopic, and dissolves in water to an alkaline solution, which has only a weakly reducing action on potassium permanganate. It gives a characteristic yellow to brownish-red colour when warmed with nitric acid. When treated with sulphuric acid, the compound gives hydrogen and boron hydrides.

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[38] A. Stock and E. Kuss, *Ber.*, 1914, **47**, 810; *A.*, ii, 359.

Sodium hypoborate, $NaOBH_3$, was also prepared, and found to possess properties similar to those of the potassium salt. No insoluble hypoborates could be obtained by mixing a solution of the potassium or sodium salt with those of other metallic salts.

The reactions described in this paper are exactly analogous to those described by Travers and Ray.[39]

Two papers have appeared dealing with work on scandium.[40,41]. Many new salts of this element are described, and also the extraction and purification of the oxide from wolframite. It is hardly necessary to specify the new salts that have been prepared, but a point of some interest is raised in the fractional separation of the scandium from thorium, yttrium, and ytterbium. An examination of 300 fractions showed that scandium is a uniform substance. The rose-yellow precipitate in the second analytical group was investigated, and it was found that the claim previously made, that this is due to a new element, is not justified.[42, 43] This sulphide was obtained in large quantities, and was proved to consist of copper sulphide with small quantities of tin and tungsten sulphides, together with much sulphur.

Aluminium nitride[44] has been obtained in colourless, hexagonal needles by heating the crude compound at 2010—2030° in a tube heated in a carbon resistance furnace in the presence of excess of nitrogen. The compound dissociates when heated at atmospheric pressure at 1850°.

Mention was made last year of a paper in which doubt was thrown on the existence of the aluminates as definite chemical compounds. This was controverted in a later paper. Two further papers[45, 46] have since appeared by the same authors, and the question as to the existence of aluminates seems to have been decided in a third paper.[47] Conductivity measurements show that such compounds must exist, for the measurements are definitely against the assumption of colloidal aluminium hydroxide. Moreover, when hydrolysis takes place, the aluminium hydroxide is deposited in the crystalline form. The arguments, therefore, are strongly in favour of the existence of aluminates as true chemical compounds.

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[39] M. W. Travers and R. C. Ray, *Proc. Roy. Soc.*, 1912, [*A*], **87**, 163 ; *A.*, 1912, ii, 938.

[40] R. J. Meyer and, in part, A. Wassjuchnov, N. Drapier, and E. Bodländer, *Zeitsch. anorg. Chem.*, 1914, **86**, 257 ; *A.*, ii, 269.

[41] J. Sterba-Böhm, *Zeitsch. Elektrochem.*, 1914, **20**, 289 ; *A.*, ii, 565.

[42] M. Ogawa, *J. Coll. Sci. Tōkyō*, 1908, **25**, xv, 1 ; xvi, 1 ; *A.*, 1908, ii, 952, 953.

[43] A. Skrabal and P. Artmann, *Chem. Zeit.*, 1909, **33**, 143 ; *A.*, 1909, ii, 243.

[44] J. Wolf, *Zeitsch. anorg. Chem.*, 1914, **87**, 120 ; *A.*, ii, 568.

[45] E. G. Mahin, *J. Amer. Chem. Soc.*, 1914, **36**, 2381 ; *A.*, ii, 850.

[46] W. Blum, *ibid.*, 2383 ; *A.*, ii, 850.

[47] R. E. Slade and W. G. Polack, *Trans. Faraday Soc.*, 1914, **10**, 150 ; *A.*, ii, 811.

Group IV.

In the Report for 1912, the preparation of carbon subsulphide, C_3S_2, was referred to, this compound being produced by maintaining an arc between a graphite cathode and an anode of graphite and antimony under carbon disulphide. By somewhat similar methods, carbon sulphidotelluride, CSTe,[48] and carbon sulphidoselenide, CSSe,[49] have been obtained. In the case of the former, the graphite and antimony electrode is replaced by one containing 10 or more parts of graphite to 100 parts of tellurium. The carbon disulphide is then found to contain non-volatile decomposition products of carbon disulphide, and the compounds C_3S_2 and CSTe, which are volatile with the carbon disulphide vapour. The separation of these two compounds proved to be a very difficult matter, owing to the extreme ease with which the sulphidotelluride decomposes. It was effected by a combination of two methods, namely: (1) the repeated fractional extraction of the C_3S_2 from the solution by carbon disulphide vapour, and (2) the conversion of the C_3S_2 into thiomalononaphthylamide by its reaction with β-naphthylamine. The dilute solution of the sulphidotelluride, after drying with phosphoric oxide, was concentrated on the water-bath to a strength of 5—10 per cent., using a Hahn fractionating column. The solution was fractionally distilled at $-30°$ under very diminished pressure in a specially designed apparatus,[50] and the pure sulphidotelluride was obtained in yellowish-red crystals, melting at $-54°$ to a brilliant red liquid of high refractive power. Molecular-weight determinations with benzene and carbon disulphide as solvents gave values between 176 and 181, theory 172. The compound decomposes very rapidly at room temperature, and is exceedingly sensitive to light, decomposition taking place even at $-50°$. No evidence could be obtained of the existence of carbon ditelluride, CTe_2.

The sulphidoselenide, CSSe, was obtained in a similar way, the anode consisting of 17·5 parts graphite to 100 parts selenium. The compound was more readily isolated, owing to its greater stability. At room temperature the sulphidoselenide forms an intense yellow liquid, stable in air, and possessing a pungent odour of onions. It does not take fire when brought into contact with the flame, although the vapour of the boiling liquid burns with a beautiful lilac flame. It melts at −85°, and boils at 84°, the vapour pressure at 10° being 45 mm. It is decomposed by light and on long keeping at room temperature, but is much more stable than the sulphidotelluride. No evidence was obtained of direct union between carbon and selenium by passing selenium vapour over carbon at 1000°, neither was it found possible in any way to prepare carbon diselenide, CSe_2.

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[48] A. Stock and P. Praetorius, *Ber.*, 1914, **47**, 131; *A.*, ii, 199.

[49] A. Stock and E. Willfroth, *ibid.*, 144; *A.*, ii, 200.

[50] A. Stock, *ibid.*, 154; *A.*, ii, 171.

Some doubt has been thrown on the constitution of white lead,[51] the view being expressed that it is not a true basic carbonate of the formula $2PbCO_3,Pb(OH)_2$. In one paper a description is given of a process by which white lead is obtained by spraying basic lead acetate solution a number of times through an atmosphere of carbon dioxide. The solid which separates at first has the constitution $PbCO_3,Pb(OH)_2$; on continued action of the carbon dioxide, this solid absorbs the gas, passing through the stage

$$2PbCO_3,Pb(OH)_2,$$

and finally becomes $PbCO_3$. The increase in the percentage of carbon dioxide in the solid is gradual, and there is no evidence of any break in the continuity at the stage $2PbCO_3,Pb(OH)_2$. Lead hydroxide is soluble in an aqueous solution of sucrose, but in no stage in the above process is there any loss in weight when the solid is treated with sucrose solution. This dismisses the possibility that the solid phase is a mixture of lead carbonate and lead hydroxide. Further, a mixture of the compound $PbCO_3,Pb(OH)_2$ and lead carbonate in the correct proportions exhibits the same properties, both physically and as a pigment, as does ordinary white lead.

Further evidence is adduced in the second paper, for it is shown that lead carbonate, when agitated with a solution of basic lead acetate, withdraws lead hydroxide. Again, in the case of the basic carbonate, $PbCO_3,Pb(OH)_2$, the percentage of carbon dioxide can be increased or decreased at will by agitation with neutral or basic lead acetate solution.

Analogous results were obtained with basic zinc carbonate, precipitated calcium carbonate, precipitated barium sulphate, and precipitated barium carbonate, for these compounds on agitation with basic lead acetate solution gave $ZnCO_3,Zn(OH)_2,3Pb(OH)_2$, $2CaCO_3,Pb(OH)_2$, $3BaSO_4,Pb(OH)_2$, and $3BaCO_3,2Pb(OH)_2$ respectively. The barium carbonate and zinc carbonate compounds equal white lead in their properties as pigments. Finally, the fact that white lead loses lead hydroxide when treated with ammonium chloride solution shows that it is more loosely combined than would be expected of a true basic salt. The view is put forward that white lead is an adsorption compound of lead carbonate and lead hydroxide.

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[51] E. Euston, *J. Ind. Eng. Chem.*, 1914, **6**, 202, 382; *A.*, ii, 366, 465.

An interesting method of decomposing natural phosphates and silicates has been described.[52] The powdered mineral is heated in carbonyl chloride vapour, the anhydrous metallic chloride being formed in each case. The natural phosphates, vivianite, pyromorphite, uranite, and monazite, are attacked at temperatures between 300° and 500°, whilst the silicates, such as thorite, gadolinite, cerite, and zircon require temperatures of above 1000°. Emerald, however, is not decomposed at 1400°.

Group V.

An investigation of the dissociation of gaseous nitrogen trioxide[53] shows that the equilibrium conditions are somewhat complex, and not to be represented by the two equations

$$N_4O_6 \rightleftarrows N_2O_4 + 2NO \text{ and } N_2O_4 \rightleftarrows 2NO_2.$$

The pressure-volume relation has been determined for various temperatures and volumes of the gas, and ten alternative sets of equations are considered in reference to the data thus obtained. The final conclusion is drawn that liquid nitrogen trioxide at low temperatures consists mainly of N_4O_6 molecules, together with some N_2O_4, NO_2, and NO molecules, according to the extent of the drying. The vapour consists of a mixture of N_4O_6, N_2O_3, NO_2, and NO molecules, reacting according to the equation

$$N_4O_6 \rightleftarrows N_2O_3 + NO_2 + NO,$$

mixed with some wet N_2O_4, NO_2, and NO molecules. The effect of the prolonged drying of the liquid appears to be to enable the NO_2 and NO molecules to combine to give N_4O_6, which in the dry state dissociates to N_2O_3, NO_2, and NO in equal volumes, the N_2O_3 not further dissociating. It further seems likely that N_4O_6 molecules in the liquid state are blue, and that in the gaseous state both N_4O_6 and N_2O_3 are colourless, or nearly so. Ordinary wet nitrogen trioxide is green, owing to the mixture of blue N_4O_6 with a relatively large amount of wet NO_2. The green colour is due to the yellow molecules of NO_2 mixed with the blue N_4O_6. At very low temperatures all specimens of the liquid become quite blue, which is no doubt due to the fact that at these temperatures the yellow NO_2 molecules completely associate to give the colourless N_2O_4, which would no longer produce the green colour with the blue N_4O_6.

Some measurements have been published of the vapour pressure of solid nitrogen peroxide between $-100°$ and $-34°$.[54] The dynamical method was employed, the amount of vapour diffusing into a known volume of hydrogen being determined. The vapour pressures lie between 0·0023 mm. at $-100°$ and 39·24 mm. at $-30°$, and they are expressed by the curve

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[52] J. Barlot and E. Chauvenet, *Compt. rend,*, 1913, **157**, 1153 ; *A.*, ii, 49.

[53] B. M. Jones, *T.*, 1914, **105**, 2310.

$$\log p = \overline{14}{\cdot}9166 + \theta(0{\cdot}0604).$$

Measurements were made between $-40°$ and $-60°$ by a statical method, and these are in good agreement.

When a solution of ammonium phosphate (1·6 grams in 25 c.c. of water) is added to a solution of 1 gram of ferrous chloride in 20 c.c. of alcohol saturated with nitric oxide at 0°, the whole operation being carried out in an atmosphere of nitric oxide, a blackish-brown, viscid oil is precipitated, which crystallises when cooled in a freezing mixture.[55] The substance was obtained pure in the form of brown, flaky crystals, and has the formula $Fe(NO)HPO_4$. Freshly precipitated ferrous phosphate also absorbs nitric oxide to give the same compound. Copper sulphate, chloride, and bromide combine with nitric oxide according to the reversible action

$$CuR_2 + NO \rightleftarrows CuR_2NO.$$

The combination takes place in alcoholic solution, the presence of water greatly diminishing the combination. Migration experiments showed that the brown, ferrous nitric oxide compounds contained the complex cation $(FeNO)^{\cdot\cdot}$, whereas in the green compounds a complex ferrous anion exists. The combination with nitric oxide seems to be characteristic of the normal ferrous and cupric compounds, and not of those in which the metal is present in a stable, complex ion.

A study of the phase diagram of the system ammonia and water has revealed the existence of two compounds, $2NH_3,H_2O$ and NH_3,H_2O, which melt at $-78·9°$ and $-79·0°$ respectively.[56] The eutectic point at which ammonia and the compound $2NH_3,H_2O$ co-exist as solid phases lies at 81·4 mols. per cent. of ammonia and $-92·5°$. The point at which $2NH_3,H_2O$ and NH_3,H_2O co-exist lies at 58·5 per cent. of ammonia and $-86°$, and that corresponding with the co-existence of NH_3,H_2O and ice at 34·7 per cent. of ammonia and $-100·3°$.

Solutions of alkali or other chlorates, bromates or iodates, and of hydrazine salts, may be mixed, and even boiled, without any reaction taking place.[57] If, however, a piece of tarnished copper wire or a fragment of cupric oxide is introduced into a cold solution of potassium chlorate and hydrazine nitrate, nitrogen is evolved. The reaction is accelerated by warming, and is quantitative in accordance with the equation

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[54] A. C. G. Egerton, *T.*, 1914, **105**, 647.

[55] W. Manchot, *Ber.*, 1914, **47**, 1601; *A.*, ii, 567.

[56] A. Smits and S. Postma, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 182; *A.*, ii, 808.

[57] W. R. E. Hodgkinson, *J. Soc. Chem. Ind.*, 1914, **13**, 815; *A.*, ii, 771.

$$2KClO_3 + 3N_2H_4,HNO_3 = 6H_2O + 3N_2 + 3HNO_3 + 2KCl.$$

The method may be used for the estimation of chlorates, bromates, and iodates. A slight excess of hydrazine salt is used, and the excess is destroyed by potassium permanganate and nitric acid, when the resulting chloride, bromide, or iodide can be estimated.

A considerable amount of work has been done on the nitrogen derivatives of sulphurous and sulphuric acids. By the action of sulphur dioxide on ammonia in ethereal solution, amidosulphinic acid, $NH_2{\cdot}SO_2H$, or its ammonium salt, $NH_2{\cdot}SO_2NH_4$, is formed, according as to whether the sulphur dioxide or ammonia is in excess.[58] The free acid is a pale yellow compound, whilst the ammonium salt is a white substance. The compound $N_4H_{12}S_5O_{10}$, previously described by Divers and Ogawa, has been found not to exist; the substance originally prepared was impure ammonium trithionate.[59]

Hydroxylamine*iso*monosulphonic acid, $NH_2{\cdot}O{\cdot}SO_2{\cdot}OH$, was first indicated by Raschig in the product formed by hydrolysis of hydroxylamine*iso*disulphonic acid by hydrogen chloride.[60] This compound has now been obtained by the action of chlorosulphonic acid on hydroxylamine hydrochloride at room temperature.[61] It separates from a mixture of ether and methyl alcohol as a microcrystalline powder; it liberates iodine from potassium iodide, and is hydrolysed in acid solution to hydroxylamine.

Hydrazine hydrazinesulphonate has been obtained by aspirating air first through a flask containing fuming sulphuric acid of high anhydride content, and then through a flask containing anhydrous hydrazine.[62] Considerable quantities of the salt are formed in accordance with the equation $2N_2H_4 + SO_3 = H_2N{\cdot}NH{\cdot}SO_3H,N_2H_4$. The product is dissolved in water and heated with excess of barium hydroxide in order to expel the unchanged hydrazine, the excess of barium is precipitated with carbon dioxide, and the filtrate from the barium carbonate is evaporated in a vacuum. A residue of barium hydrazinesulphonate, $(N_2H_3{\cdot}SO_3)_2Ba,2H_2O$, is left, which may be obtained in glistening needles by solution in water and precipitation with alcohol. The calcium salt, $(N_2H_3{\cdot}SO_3)_2Ca,H_2O$,

[58] M. Ogawa and S. Aoyama, *Sci. Reports Tôhoku Imp. Univ.*, 1913, **2**, 121; *A.*, ii, 264.

[59] E. Divers and M. Ogawa, *T.*, 1901, **79**, 1102.

[60] F. Raschig, *Annalen*, 1887, **241**, 161.

[61] F. Sommer and H. G. Templin, *Ber.*, 1914, **47**, 1221; *A.*, ii, 458.

[62] W. Traube and O. Vockerodt, *ibid.*, 938; *A.*, ii, 358.

and the strontium salt, $(N_2H_3{\cdot}SO_3)_2Sr,2H_2O$, can be obtained in a similar way.

By double decomposition, using the barium salt and ammonium carbonate, ammonium hydrazinesulphonate, $N_2H_3{\cdot}SO_3NH_4$, was obtained as a deliquescent, crystalline mass. This salt is isomeric with hydrazine amidosulphonate.[63]. The potassium salt,

$$N_2H_3{\cdot}SO_3K,$$

and the sodium salt, $N_2H_3{\cdot}SO_3Na,H_2O$, were prepared in a similar way from potassium and sodium sulphates. The former crystallises in needles and the latter in monoclinic tablets. All these salts are stable in alkaline and in neutral solution, but are decomposed by acid into hydrazine and sulphuric acid. From the barium salt and silver nitrate, the silver salt, $N_2H_3{\cdot}SO_3Ag$, was obtained in beautiful, glistening needles. From the barium salt, by the action of sulphuric acid, the free acid, $N_2H_3{\cdot}SO_3H$, was obtained in glistening needles, which melt and decompose at 217°.

If a strongly cooled, aqueous solution of potassium nitrite is treated with finely powdered hydrazinesulphonic acid, the following reaction takes place:

$$NH_2{\cdot}NH{\cdot}SO_3H + KNO_2 = 2H_2O + N_3SO_3K.$$

From the resulting solution the salt, potassium azoimidesulphonate, has been obtained. It crystallises in long, flat prisms, which explode on heating. The corresponding sodium, ammonium, and barium salts have been obtained in a similar way.

Group VI.

Pure perchromic acid has been prepared by the interaction of chromium trioxide and 97 per cent. hydrogen peroxide in methyl ether solution at $-30°$.[64] The reaction takes place according to the equation

$$2CrO_3 + 7H_2O_2 = 2H_3CrO_8 + 4H_2O.$$

The blue solution was poured off the excess of either chromium trioxide or hydrogen peroxide, dried over phosphoric oxide, and then evaporated in a vacuum at $-30°$, when the acid was obtained as a dark blue, crystalline mass, which decomposes a few degrees above $-30°$. Analysis shows that it has the formula $H_3CrO_8,2H_2O$, the water being water of constitution. The red perchromates are considered to be anhydro-salts of the blue perchromic acid, their constitution being $\begin{matrix}O\\O\end{matrix}\!\!\gg Cr(O{\cdot}OM)_3$, whilst that of the acid is $(HO)_4Cr(O{\cdot}OH)_3$.

It is found that by the action of sulphuric acid on calcium fluoride it is impossible to obtain hydrogen fluoride of a greater strength than 95—96 per cent.[65 66]. The best yield is obtained with 90 per cent. sulphuric acid. When pure sulphuric acid is used, fluorosulphonic acid may be produced, and a quantitative yield of this acid may readily be obtained by heating calcium fluoride with fuming sulphuric acid containing 60 per cent. of the anhydride. The reaction takes place according to the equation

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[63] A. P. Sabanéev, *J. Russ. Chem. Soc.*, 1899, **31**, 375; *A.*, 1900, ii, 13.

[64] E. H. Riesenfeld and W. Mau, *Ber.*, 1914, **47**, 548; *A.*, ii, 279.

$$CaF_2 + H_2SO_4 + 2SO_3 = CaSO_4 + 2F{\cdot}SO_2{\cdot}OH.$$

Sodium fluorosulphonate may readily be obtained by heating the acid with sodium chloride in a platinum retort under reflux. Boiling alcohol extracts the sodium fluorosulphonate, and, on cooling, this salt separates in iridescent plates or needles.

Fluorosulphonic acid is decomposed on boiling with sulphur according to the equation

$$2F{\cdot}SO_2{\cdot}OH + S = 3SO_2 + 2HF.$$

Group VII.

A thermal analysis of mixtures of bromine and water leads to the conclusion that the composition of the hydrate of bromine is $Br_2,8H_2O$.[67] The crystals were centrifuged on kaolin at 0° in order to free them from any adhering bromine or water, and were then analysed. The analytical results confirm the correctness of the above formula.

An interesting study has been made of the relative stability of pure calcium hypochlorite, bleaching powder, and a mixture of calcium hypochlorite and calcium chloride.[68] Towards dry air, free from carbon dioxide, calcium hypochlorite and bleaching powder show very little difference in behaviour at 90°, there being only a slight loss of chlorine in each case. In moist air containing carbon dioxide at room temperature, bleaching powder loses more of its available chlorine than does the hypochlorite. The mixture of hypochlorite and chloride behaves similarly to bleaching powder. In an atmosphere of dry carbon dioxide, calcium hypochlorite loses a small percentage of its available chlorine after five hours' exposure; the mixture of hypochlorite and chloride loses a slightly greater percentage, whilst bleaching powder loses all its available chlorine. In moist carbon dioxide, both the hypochlorite and bleaching powder lose all their available chlorine; the former, however, gives hypochlorous acid as well as chlorine, whilst the latter only evolves chlorine. With ammonia, both calcium hypochlorite and bleaching powder give an almost quantitative yield of nitrogen.

[65] O. Ruff and H. J. Braun, *Ber.*, 1914, **47**, 646; *A.*, ii, 263.

[66] O. Ruff, *ibid.*, 656; *A.*, ii, 263.

[67] H. Giran, *Compt. rend.*, 1914, **159**, 246; *A.*, ii, 723.

[68] K. A. Hofmann and K. Ritter, *Ber.*, 1914, **47**, 2233; *A.*, ii, 612.

Group VIII.

Some attention has been paid to the question of the sorption of hydrogen by palladium.[69, 70, 71, 72] The curves obtained by plotting the rate of solution as a function of the quantity of gas occluded consists of two portions, indicating the occurrence of two distinct processes.[70] The suggestion is made that there are two modifications of palladium, which differ very considerably in respect of their activity towards hydrogen. The first portion of the velocity-concentration curve, on this view, is mainly determined by the active form, whilst the second portion refers to the sorption of the hydrogen by the less active form. When palladium-black is used, a smooth curve is obtained, and the suggestion follows that this material consists almost entirely of the active form. A somewhat similar view is put forward in the idea that palladium consists of a crystalline form and an amorphous form, the latter being the more active.[71]

Analogous results were obtained in a series of measurements of the electrical conductivity and the density of palladium wires containing measured amounts of occluded hydrogen.[72]

Some experiments have been carried out on the nature of precipitated nickel sulphide.[73] It appears that there are three different modifications, which differ in respect of their solubility in acids. The precipitates from a neutral solution of nickel chloride and soluble sulphides consist mainly of a modification which dissolves readily in acids. The less soluble modification is formed by boiling with water, or by long contact with a cold solution containing nickel, or with cold dilute acetic acid. All the modifications have the same composition, NiS, and the most soluble is the most readily oxidised by air.

α-Nickel sulphide is soluble in mineral acids down to $0{\cdot}01N$, whilst β-nickel sulphide is fairly rapidly dissolved by $2N$-hydrochloric acid, and the γ-modification is not appreciably dissolved except on addition of oxidising agents. The differences in solubility are too great to be explained by colloidal conditions, and must be due to polymerisation.

E. C. C. BALY.

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[69] F. Halla, *Zeitsch. physikal. Chem.*, 1914, **86**, 496; *A.*, ii, 178.

[70] A. Holt, *Proc. Roy. Soc.*, 1914, [*A*], **90**, 226; *A.*, ii, 452.

[71] A. Sieverts, *Zeitsch. physikal. Chem.*, 1914, **88**, 103; *A.*, ii, 626.

[72] G. Wolf, *ibid.*, 1914, **87**, 575; *A.*, ii, 517.

[73] A. Thiel and H. Gessner, *Zeitsch. anorg. Chem.*, 1914, **86**, 1; *A.*, ii, 277

ORGANIC CHEMISTRY.

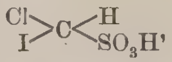
PART I.—ALIPHATIC DIVISION.

THE fact that a considerable proportion of the original literature was no longer available during the second half of the past year has had comparatively little effect on the compilation of this section of the Annual Report. The total number of papers reviewed has been about the average, and the quality of the work described has been well maintained, but, for obvious reasons, very little progress has been made in some of the new developments which were described last year. Nevertheless, many important advances have been made on systematic lines, although, in some branches of the subject, a number of novel results have been described, which are isolated observations, and therefore unsuitable for general discussion. Taking these factors into account, it has been considered advisable to limit the number of topics reviewed in the Report, and to deal with these in somewhat greater detail than is possible in normal circumstances.

Optical Activity.

The preparation of optically active compounds and the continuation of attempts to correlate rotatory power with constitution are still being continued with unabated vigour, so that new facts and new theories have rapidly accumulated during the past year. As quantitative work on optical activity is naturally carried out on compounds of simple type, the subject is one which may be appropriately discussed under the general heading of aliphatic compounds. Considering the number of papers to be reviewed, attention will be restricted in the following account to cases in which activity is dependent on the presence of "asymmetric carbon atoms" only.

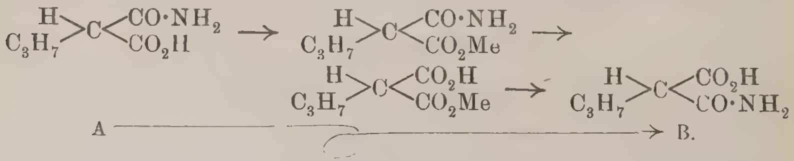
In the first place, attention may be directed to the satisfactory solution of a problem of long standing. The question has often been raised as to the simplest possible type of organic compound which should be capable of displaying optical activity, and it has now been shown that when a single carbon atom is united to three different elementary atoms and to an inorganic radicle, the resulting molecule can exist in active forms. The compound to furnish this interesting result was chloroiodomethanesulphonic acid,



$$\genfrac{}{}{0pt}{}{Cl}{I}\!>\!C\!<\!\genfrac{}{}{0pt}{}{H}{SO_3H},$$

and it is noteworthy that the activity, which was measured on the ammonium salt, was not impaired by the action of the usual racemising agents.[1]

Turning to another problem of fundamental importance, a most instructive transformation is reported by Fischer, who has, after considerable difficulty, succeeded in interchanging two groups attached to the same asymmetric carbon atom, so that an optical inversion has now been established in which all the intermediate compounds have been isolated.[2] *d-iso*Propylmalonamic acid was, in the first place, converted into the methyl ester, and the amino-group expelled by the action of nitrous acid. Thereafter, through the intermediate formation of the corresponding hydrazidic acid, the esteric methoxyl group was replaced by the amino-group, and, in this way, the desired interchange of two groups was completed with the result, already indicated, that the *l*-isomeride of the original acid was formed. Inspection of the structural scheme illustrating this cycle of changes will show that the attachment of the four groups to the asymmetric carbon atom remains undisturbed during the various reactions, and that at no stage is any group, directly attached to the asymmetric atom, completely removed:



$$\genfrac{}{}{0pt}{}{H}{C_3H_7}\!>\!C\!<\!\genfrac{}{}{0pt}{}{CO{\cdot}NH_2}{CO_2H} \longrightarrow \genfrac{}{}{0pt}{}{H}{C_3H_7}\!>\!C\!<\!\genfrac{}{}{0pt}{}{CO{\cdot}NH_2}{CO_2Me} \longrightarrow \genfrac{}{}{0pt}{}{H}{C_3H_7}\!>\!C\!<\!\genfrac{}{}{0pt}{}{CO_2H}{CO_2Me} \longrightarrow \genfrac{}{}{0pt}{}{H}{C_3H_7}\!>\!C\!<\!\genfrac{}{}{0pt}{}{CO_2H}{CO{\cdot}NH_2}$$

$$A \longrightarrow B.$$

The change from A to B thus constitutes an inversion, as indicated by the looped arrow, a convenient expression which will be found useful in blackboard illustration.[3]

Reference may, at this stage, be made to another idea which may likewise be of service in teaching, and that is a revival of the suggestion that racemisation, even in the case of acids, is merely a particular case of tautomeric change, and is due to the oscillation of a labile hydrogen atom.[4] There is much to be said for this suggestion, particularly as the best defined examples of autoracemisation occur in the case of compounds which are definitely tautomeric, but nevertheless an explanation of racemisation which would be perfectly general in its application is still to be found.

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[1] W. J. Pope and J. Read, *T.*, 1914, **105**, 811.

[2] E. Fischer and F. Brauns, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 714; *A.*, i, 942.

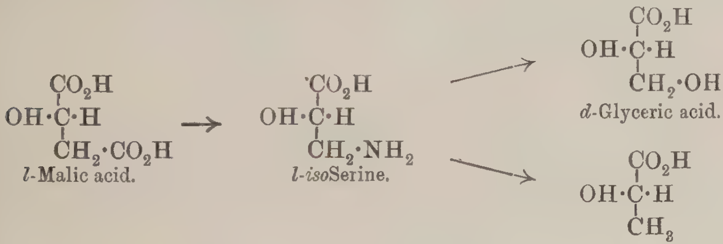
[3] P. F. Frankland, *T.*, 1913, **103**, 741.

[4] O. Rothe, *Ber.*, 1914, **47**, 843; *A.*, i, 538.

Several publications of the past year deal with the allocation of definite configurations to a number of aliphatic compounds. It is, of course, notorious that the vagaries of the Walden inversion must still render uncertain speculations on configuration which are based upon reactions involving substitution and replacement of groups. At the same time, an interesting series of transformations has resulted in the determination, with some degree of certainty, of the configurations to be assigned to the active glyceric and lactic acids.[5] Starting with the amide of *l*-malic acid, the corresponding amic acid was prepared and converted into *l*-*iso*serine,

$$CO_2H \cdot CH(OH) \cdot CH_2 \cdot NH_2.$$

From this, in turn, *d*-lactic and *d*-glyceric acids were obtained, the former by a somewhat indirect process, and the claim is made that the respective configurations of the various compounds involved must be as represented below:



l-Malic acid. *l*-*iso*Serine. *d*-Glyceric acid. *d*-Lactic acid.

These views can certainly be supported by a number of arguments, and the scheme of the research is ingenious, but, considering the nature and variety of the reagents involved, it seems unlikely that the transformations are entirely unaccompanied by changes in configuration.

In reviewing the numerous publications which have appeared during the past twenty years regarding the relationship between constitution and molecular rotation, one cannot fail to be impressed with the great changes which have taken place in the experimental methods employed and in the selection of suitable compounds for examination. As a result of many patient investigations, due recognition is now given in accurate work to the effect of temperature, concentration, the nature of the solvents used, dispersion effects, and other important factors, whilst the attention now paid to racemisation affords a better guarantee that optically pure compounds are used. Perhaps the most prominent feature of recent work in this field is the large number of optically active compounds which have been examined, and the completeness with which homologous series of these compounds have been built up on systematic lines. The pages of the Journal bear striking testimony to this point in the consecutive investigations described by Pickard and Kenyon. Obviously, work of this magnitude and detail can only be studied and appreciated by reference to the original papers, but a brief summary of the present position of the subject may be given, as a number of definite advances have recently been made.

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[5] K. Freudenberg, *Ber.*, 1914, **47**, 2027; *A.*, i, 924.

In the first place, it should be mentioned that, in continuation of his previous work, Lowry has examined the magnetic rotatory dispersion of a large number of organic compounds which, for the most part, are of simple type.[6] It is found that, generally speaking, the values determined are remarkably constant in homologous series. On the other hand, optical rotatory dispersion is more variable,[7] although, in the case of disubstituted carbinols of the aliphatic series, the value becomes constant when, in a homologous series, the fraction of the molecule in which the chain is lengthened becomes the heaviest part of the asymmetric system. Further, it has been shown that the formula $a = k/(\lambda^2 - \lambda_0^2)$, which can be applied generally to express the rotatory dispersion of organic compounds in the homogeneous state, is consistent with the values found for active carbinols at moderate temperatures, and in some cases at all temperatures up to the boiling point of the liquids.[8] The fact that the rotatory dispersions of esters do not conform uniformly to the above formula must be accepted as indicating that ethereal salts are, after all, more liable to undergo intramolecular changes than are the carbinols, and are thus less suitable for the determination of true optical values.

This idea is supported by a study of a series of active esters of the type $CH_3 \cdot CH(O \cdot CO \cdot R) \cdot R'$, which were prepared from the corresponding active carbinols.[9] The examination of numerous examples of these esters has included the effect of temperature, change of concentration, the influence of solvents, and the determination of the rotations in light of different wave-lengths. The main conclusions drawn are: (1) alterations in rotatory power observed owing to change of temperature or the conditions of solution, are due to alteration in the nature or complexity of the active molecules, and (2) the anomalous dispersion exhibited by some esters of apparently simple structure points to the occurrence of intramolecular changes in the ester group. This supposed change apparently cannot involve alteration in mass, and is probably distinct from association or polymerisation. One suggestion offered is that the ester group may, in common with the carboxyl group, react either as

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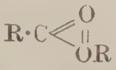
[6] T. M. Lowry, *T.*, 1914, **105**, 81.

[7] T. M. Lowry, R. H. Pickard, and J. Kenyon, *ibid.*, 94.

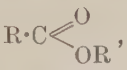
[8] R. H. Pickard and J. Kenyon, *ibid.*, 1115.

[9] *Ibid.*, 830, 2262; J. Kenyon, *ibid.*, 2226.



$\mathrm{R{\cdot}C}<\begin{matrix}\mathrm{O}\\ \| \\ \mathrm{OR}\end{matrix}$

or



$\mathrm{R{\cdot}C}<\begin{matrix}\mathrm{O}\\ \mathrm{OR}\end{matrix}$,

the proportion of each form varying according to the conditions, although the authors are careful to state that they obtained no direct evidence indicating the presence of such isomerides in the esters examined by them. The results of this and other researches[10] afford strong support to the recent expansion of the idea that anomalous dispersion is due to the simultaneous presence of two interconvertible active compounds possessing different dispersive powers.[11]

Evidently a new feature of complexity must now be recognised in quantitative investigations connected with optical activity. Optically pure liquids must be examined under conditions when they are actually homogeneous, and this, no doubt, will play a prominent part in the future development of this important subject.

Considering the manifold difficulties which surround this problem, it is surprising to find that, even in compounds which contain several asymmetric systems, some empirical quantitative generalisations have been established. Among these may be mentioned Hudson's rule regarding molecular rotation in the sugar group.[12] Although this generalisation is based on principles which are not generally accepted, it has been shown to apply exactly in the case of the α- and β-forms of monomethyl glucose.[13] As these isomerides showed suspended mutarotation, it was possible to determine the maximum optical values directly, the results obtained being in agreement, within the limits of experimental error, with the values calculated by Hudson's method.

It is possible that the whole subject of optical activity may, in the near future, undergo startling changes, and much interest will be taken in the results recently contributed by Erlenmeyer and his collaborators on asymmetric syntheses effected by means of "asymmetric induction." The well-known experiments quoted by

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[10] G. W. Clough, *T.*, 1914, **105**, 49.

[11] H. E. Armstrong and E. E. Walker, *Proc. Roy. Soc.*, 1913, [*A*], **88**, 388 ; *A.*, 1913, ii, 543.

[12] *Ann. Report*, 1909, 124 ; 1913, 79.

[13] J. C. Irvine and T. P. Hogg, *T.*, 1914, **105**, 1386.

Marckwald, in which active α-methylbutyric acid was obtained by decomposing the brucine hydrogen salt of methylethylmalonic acid, have been repeated under conditions which exclude the separation of the salt in fractions. The ultimate product obtained nevertheless displayed optical activity, and this result is interpreted by Erlenmeyer as a proof that two isomeric methylethylmalonic acids exist, and that the formation of an active methylbutyric acid is due to induction. Further, *d*- or *l*-tartaric acid may take the place of brucine in a parallel reaction, giving rise similarly to the *l*- or *d*-form of methylbutyric acid.[14] Results which are less easily explained have, in addition, been reported, as cinnamic acid is said to have been obtained in *d*- and *l*-forms by heating with the active tartaric acids.[15] According to Erlenmeyer, cinnamic acid is to be regarded as $C_6H_5{\cdot}CHL{\cdot}CHL{\cdot}CO_2H$, where L represents an unoccupied valency power the existence of which permits of the formation of non-superimposable forms. Scrutiny of the experimental details leaves a certain amount of doubt as to whether the important claim has been justified that a compound devoid of an asymmetric atom (or its equivalent) has actually been obtained in active forms, or, at all events, has been caused to acquire optical activity. At the same time, the idea does not rest on the evidence of a single example, as benzaldehyde has also been added to the list of compounds which can be made to display induced activity.[16] The development of this work will doubtless be closely watched.

Tautomerism.

Although in recent Reports considerable attention has been given to the consideration of tautomeric change, and the subject has also been reviewed in the latest Presidential Address,[17] it is difficult to resist the temptation to refer to some new observations which seem worthy of mention.

The suggestion that ozone will prove to be a useful reagent in the study of tautomerides has been considerably strengthened in the course of the past year, and in an important paper[18] a number of fresh examples illustrating its efficiency are quoted. In addition, evidence has now been accumulated to show that ozone does not act catalytically in affecting the keto-enol change, and that its reaction is confined strictly to enolic forms. Now that these points have been established, the method will doubtless be extensively used, particularly as the experimental procedure appears to be comparatively simple. In the paper referred to, the results quoted are for the most part perfectly normal and in agreement with those arrived at by other methods, but one or two special cases are considered. Thus, the mixture of ozonides obtained from oxalacetone gave, on decomposition, a variety of products the nature of which proves that the parent diketone exists in three unsaturated forms, two being mono-enolic and the third di-enolic:

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[14] E. Erlenmeyer and F. Landsberger, *Biochem. Zeitsch.*, 1914, **64**, 366; *A.*, i, 920.

[15] E. Erlenmeyer, G. Hilgendorff, and F. Landsberger, *ibid.*, 296; *A.*, i, 965.

[16] *Ibid.*, 382; *A.*, i, 967.

[17] W. H. Perkin, jun., *T.*, 1914, **105**, 1176.

[18] J. Scheiber and P. Herold, *Annalen*, 1914, **405**, 295; *A.*, i, 926.

$$\mathrm{COMe{\cdot}CH{:}C(OH){\cdot}CO_2Et,\quad OH{\cdot}CMe{:}CH{\cdot}CO{\cdot}CO_2Et,\quad OH{\cdot}CMe{:}C{:}C(OH){\cdot}CO_2Et.}$$

In view of this result, and others of a similar nature, it is not surprising that the application of Meyer's volumetric method to diketones frequently gives figures pointing to an enol content of nearly 100 per cent., and, in the case of oxalacetone, the result is above this maximum.

Nevertheless, Meyer's process continues to give valuable results, and, in some instances, adequate explanations have been forthcoming to account for the discrepancies occasionally encountered in comparing the values obtained by this method with those indicated by purely physical processes. Thus, on redetermining the refractive indices of pure (ketonic) acetoacetic ester, and also of the equilibrium mixture,[19] values have been obtained which are in agreement with the result previously arrived at by the titration method. The conclusion is again drawn that, in the liquid state, the equilibrium mixture contains from 7 to 7·4 per cent. of the enolic form, and as this result is considerably higher than that quoted by Knorr, it is boldly suggested that the latter worker failed to determine the refractive index of the keto-ester until it had undergone partial enolisation.

An interesting application of the bromine-titration process is indicated in a paper, where it is shown that the desmotropic changes exhibited by nitro-compounds can be followed quantitatively, just as in the case of keto-enols. Phenyldinitromethane proved a specially suitable test substance in this respect, and as the *aci*-form is more soluble than the true nitro-derivative, the effect of water and the simple alcohols is the reverse of that occasioned with tautomeric ketones.[20] Current ideas regarding the structure of *iso*nitro-compounds are, however, still somewhat unsettled.[21]

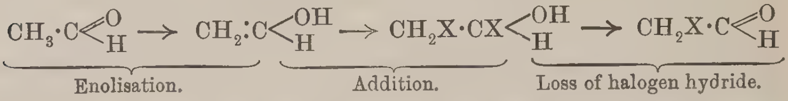
The idea that, in the case of aldehydes, substitution by means of halogens is preceded by a change comparable with the keto-enol

[19] K. H. Meyer and F. C. Willson, *Ber.*, 1914, **47**, 837 ; *A.*, i, 483.

[20] K. H. Meyer and P. Wertheimer, *ibid.*, 2374 ; *A.*, i, 1061.

[21] S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1414 ; *A.*, 1913, i, 1297.

transformation has been realised in the course of a dynamical study of the action of bromine or iodine on acetaldehyde.[22] It was found that, in the absence of acids, bromine acts entirely as an oxidising agent, but that oxidation and substitution proceed simultaneously in strongly acid solutions. The fact that the velocity of the reaction is independent of the concentration and nature of the halogen used may be accounted for on the supposition that three distinct changes are involved, the first of which is enolisation:



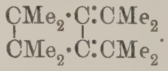
$$\underbrace{\mathrm{CH_3{\cdot}C}{\lessdot}^{\mathrm{O}}_{\mathrm{H}} \longrightarrow \mathrm{CH_2{:}C}{<}^{\mathrm{OH}}_{\mathrm{H}}}_{\text{Enolisation.}} \underbrace{\longrightarrow \mathrm{CH_2X{\cdot}CX}{<}^{\mathrm{OH}}_{\mathrm{H}}}_{\text{Addition.}} \underbrace{\longrightarrow \mathrm{CH_2X{\cdot}C}{\lessdot}^{\mathrm{O}}_{\mathrm{H}}}_{\text{Loss of halogen hydride.}}$$

It may be mentioned that, according to the most recent views,[23] the formation of iodoform from acetaldehyde is another reaction that proceeds only with the enolic form, and it will be interesting to observe how far the tendency of aldehydes to react in this manner is of general application.

Hydrocarbons.

With the exception of investigations on the mechanism of combustion, few publications of the past year have dealt with the chemistry of saturated hydrocarbons. At the present time, most researches on unsaturated hydrocarbons lead ultimately to the caoutchouc problem, with the result that it is often a matter of some difficulty to disentangle from the mass of published work results which are of general interest and importance. Several recent papers have, however, dealt with the formation of polymerides from hydrocarbons, and a number of fresh contributions have been made to this long-standing problem.

As an example of such work, attention may be directed to a careful study of tetramethylallene, $CMe_2{:}C{:}CMe_2$, which appears to have been obtained pure for the first time.[24] It is shown that on polymerisation under the simplest possible conditions the hydrocarbon is converted almost completely into the dimeride, the structure of which, in view of its optical properties, is probably



$$\begin{array}{l} \mathrm{CMe_2{\cdot}C{:}CMe_2} \\ \;|\qquad\;\;| \\ \mathrm{CMe_2{\cdot}C{:}CMe_2}. \end{array}$$

On the other hand, more drastic methods result in the formation of acetylenic derivatives, such as $CHMe_2{\cdot}CHMe{\cdot}C{:}CH$, and the alteration thus occasioned in the carbon chain points to a considerable tension in the structure $CR_2{:}C{:}CR_2$. A general principle seems to be involved here, as comparison of the velocities of polymerisation of allene, di-, tri-, and tetra-methylallene, proves that the stability of the compounds diminishes steadily with increasing substitution.[25] The limiting case is thus reached in tetramethylallene, where all the replaceable hydrogen atoms are substituted by alkyl groups.

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[22] H. M. Dawson, D. Burton, and H. Ark, *T.*, 1914, **105**, 1275.

[23] A. Pieroni and E. Tonnioli, *Gazzetta*, 1913, **43**, ii, 620 ; *A.*, i, 6.

[24] B. K. Mereshkovski, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1940 ; *A.*, i, 369.

Halogen derivatives of acetylene are now being used extensively, and in another section of the Report reference is made to a synthetical method of preparing unsaturated glycols which depends on the use of magnesium acetylene haloids.[26] Two types of such reagents are available, namely, $CH{:}C{\cdot}MgX$ and $MgX{\cdot}C{:}C{\cdot}MgX$, and the former, on reaction with ketones, give rise to unsaturated tertiary alcohols. A greater range of reactions is afforded by the use of dimagnesium acetylene dibromide, which, naturally, reacts with ketones and aldehydes to give ditertiary γ-glycols and disecondary γ-glycols respectively.[27] As a side-issue of the general scheme of research, it may be remarked that the results of this series of investigations point conclusively to the symmetrical structure for the halogen derivatives of acetylene.[28] This point was referred to last year, when it was shown that Nef's views as to the structure of these derivatives were open to criticism.

Caoutchouc.—As was to be expected, the list of patented processes for the preparation and polymerisation of hydrocarbons related to caoutchouc has been materially increased during the past year. The methods employed continue to show great diversity, and there is a natural tendency to range far and wide in search of polymerising catalysts, but, apart from this aspect of the general problem, it is evident that our ideas regarding the structure of the caoutchouc complex must, in the meantime, remain somewhat less decided than was the case a year ago. Before dealing with new experimental facts, mention may perhaps be made of an interesting historical account of the earlier work on the synthesis of caoutchouc which will be useful in teaching, provided less prominence is given to the controversial aspects of the subject.[29]

As is well known, the claim made by Harries that the caoutchoucs prepared from isoprene, by autopolymerisation, or by the action of acetic acid, are identical with each other and with the natural product, depends on the identity of the respective ozonides. A similar comparison of the caoutchoucs derived from isoprene by the action of sodium or of peroxides leads, however, to the conclusion that in each case the products are non-homogeneous.[30] From the fact that the ozonides thus obtained decompose to give succinic acid, acetonylacetone, lævulinaldehyde, and lævulic acid, it is deduced that the caoutchoucs must contain, not only 1 : 5-dimethyl-$\Delta^{1:5}$-*cyclo*-octadiene, but also the corresponding 1 : 6-dimethyl isomeride:

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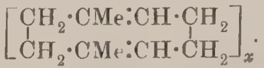
[25] S. V. Lebedev and B. K. Mereshkovski, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249 ; *A.*, 1913, i, 1285.

[26] S. I. Iocitsch, *ibid.*, 1902, **34**, 239 ; *A.*, i, 393.

[27] *Ibid.*, 242 ; *A.*, i, 405.

[28] *Ibid.*, 1904, **36**, 1545 ; *A.*, i, 373.

[29] F. J. Pond, *J. Amer. Chem. Soc.*, 1914, **36**, 165 ; *A.*, i, 194.



$$\left[\begin{array}{l} \overset{}{C}H_2\cdot CMe\colon CH\cdot CH_2 \\ \,| \qquad\qquad\qquad\quad\;\; | \\ CH_2\cdot CMe\colon CH\cdot CH_2 \end{array}\right]_x .$$

In order to explain this result, it is suggested that the different polymerides arise, respectively, from the symmetrical and the unsymmetrical condensation of two molecules of isoprene. The statement is also made that the caoutchouc prepared by autopolymerisation of isoprene is likewise a mixture, and is similar to "sodium caoutchouc," in contrast to which the natural product is derived entirely from 1 : 5-dimethyl-$\Delta^{1:5}$-*cyclo*-octadiene. According to the results of this research, the whole question of the identity or non-identity (and also of the uniformity) of artificial and natural caoutchoucs is once more thrown open. To this Harries has replied, admitting the irregularity with which the polymerisation of isoprene proceeds, but suggesting that the source of the above conflicting results may be traced to the presence of impurities in the isoprene used by Steimmig.[31] The suggestion has been followed by what might, with advantage, have preceded this discussion, namely, a redetermination and standardisation of the physical constants of the parent hydrocarbon.[32] It may, in passing, be noted that the values now quoted for the density and refractive index of isoprene are in fair agreement with those obtained by other workers.[33]

It is necessary to state that the most direct evidence in favour of the idea that the caoutchouc complex consists of an aggregate of eight carbon rings has now been withdrawn.[34] As explained in last year's Report, it is possible to degrade a "regenerated caoutchouc" by conversion into the ozonide, and treatment of the latter with water. The diketone thus obtained as the essential product was then considered to be *cyclo*-octane-1 : 5-dione, but repetition of the work on a larger scale has shown that such is not the case. The degradation, in fact, results in the formation of heptane-$\beta\zeta$-

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[30] G. Steimmig, *Ber.*, 1914, **47**, 350; *A.*, i, 307.

[31] C. Harries, *ibid.*, 573; *A.*, i, 422.

[32] *Ibid.*, 1999; *A.*, i, 917.

[33] S. V. Lebedev and B. K. Mereshkovski, *loc. cit.*

[34] C. Harries, *Ber.*, 1914, **47**, 784; *A.*, i, 386.

dione, $CH_3 \cdot CO \cdot [CH_2]_3 \cdot CO \cdot CH_3$, which readily undergoes dehydration, and this alteration in composition leads to a fortuitous agreement with the analytical figures required for $C_8H_{12}O_2$. Of the nature and identity of this diketone there can be no further doubt, as the same compound has been obtained in the course of entirely different work by the oxidation of heptan-ζ-ol-β-one by chromic acid.[35]

Although thus deprived of what appeared to be a most convincing experimental proof, the idea that caoutchouc is derived from an eight-membered ring is still strongly supported by other results. At the same time, somewhat different views are expressed in the course of an elaborate research[36] in which the mechanism of polymerisation in olefine hydrocarbons is discussed. The general method adopted in the research now under review was to study the two dimerides of isoprene, and of related hydrocarbons, as a first stage in the more complex polymerisation. The results obtained leave the impression that rigid views on the whole question are not yet justified.

Acids and Related Compounds.

As the acids of the aliphatic series have in the past been the subject of prolonged and careful investigation, it is not surprising to find that a stage has now been reached when few discoveries of far-reaching importance have to be recorded. Much of the research now being done on the simple aliphatic acids has a direct physical bearing, and, as a result, improved methods of purification and revised physical constants are frequently reported in the literature.

Another type of physico-chemical research, in which aliphatic acids are involved, may be mentioned at this stage, as, although the subject is still incompletely developed, it will, no doubt, be followed with much interest. The general inquiry as to the nature of soap solutions has been specially prominent of late, and some results of an unexpected nature have now been established. For example, the conductivities of the potassium salts of fatty acids have been determined for all compounds, with an even number of carbon atoms, from acetic acid up to stearic acid.[37] The values found are notably high, and, taken in conjunction with previous work on this subject, it is evident that high conductivity is a general feature of these salts even when the solutions approach the colloidal condition. Moreover, a determination of the degree of hydrolysis and the true alkalinity of soap solutions shows that the amount of free alkali present in such systems is insufficient to account for the conductivity values.[38] In order to explain the behaviour of these solutions as electrolytes, the suggestion is made that this may be due to the presence of highly charged aggregates which are not ions in the ordinary sense of the term, but for which the expression "colloidal ion" might reasonably be applied. Work of this nature offers many possibilities for theoretical expansion, but must present many experimental difficulties.

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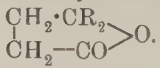
[35] R. G. Fargher and W. H. Perkin, jun., *T.*, 1914, **105**, 1353.

[36] S. V. Lebedev and B. K. Mereshkovski, *loc. cit.*

[37] H. M. Bunbury and H. E. Martin, *T.*, 1914, **105**, 417.

There is no other problem connected with unsubstituted monobasic acids which calls for special attention, but, on the other hand, the succinic acid series continues to prove an attractive field of inquiry. For a considerable time it has been evident that the analogy between phthalyl chloride and succinyl chloride is not well maintained, and that, generally speaking, the reactions of the latter compound are by no means in agreement with an unsymmetrical cyclic structure. The action of ammonia on the acid chloride certainly gives very small yields of succinamide, but it is now shown that, in the reaction with methylamine, the symmetrical product is formed to the extent of 25 per cent., and ultimately, in the case of aniline, the reaction of a similar type is quantitative.[39] In all probability, the different result obtained in these reactions is due to the superior effect of ammonia in removing the elements of hydrogen chloride from the intermediate compounds formed in each case. This is illustrated in the original paper by means of a structural scheme which dispenses with the necessity of modifying the symmetrical formula for succinyl chloride. The adoption of a similar scheme would serve to explain the observation[40] that succinyl chloride, in its reaction with zinc alkyl iodides, gives rise only to products of the lactonic type,



$\left.\begin{array}{l}CH_2\cdot CR_2\\ |\\ CH_2-CO\end{array}\right>O.$

On the whole, the accumulated evidence to which reference was made in last year's Report is in favour of the normal formula for the chlorides of all acids of the succinic type. Certainly in the case of *d*-dimethoxysuccinyl chloride the optical behaviour of the compound indicates that it possesses an open-chain structure, and that, even under the influence of powerful catalysts, it shows no tendency to undergo tautomeric change into a lactonic modification.[41] An additional example which emphasises this distinction between phthalyl and succinyl derivatives is furnished by a study of the optically active anilic acids and anils obtained from *d*-dimethoxy- and *d*-diethoxy-succinic acids respectively.[42] No *iso*-anils were isolated, and as the activity of dimethoxysuccinanil was not affected by reagents which usually induce intramolecular changes, the conclusion may reasonably be drawn that the compound is a definite chemical individual. In the same paper it is also suggested, on theoretical grounds, that Auwers' views as to the configuration of the *s*-dialkylsuccinic acids require alteration, and that the racemic modifications are not the compounds of higher, but of lower, melting point. This idea has been confirmed experimentally, as it has been shown that whereas the dimethylsuccinic acid melting at 195° is irresolvable, the isomeride of lower melting point (127°) is the racemic form, and may be resolved by the agency of triethylenediaminecobaltic bromide.[43] This result furnishes, incidentally, an example of the somewhat unexpected application of active cobaltammines in resolutions, and also indicates the caution which must be exercised in allocating meso- and racemic configurations on the basis of melting-point comparisons.

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[38] J. W. McBain and H. E. Martin, *T.*, 1914, **105**, 957.

[39] G. F. Morrell, *ibid.*, 1733.

[40] E. E. Blaise, *Compt. rend.*, 1914, **158**, 504 ; *A.*, i, 384.

[41] T. Purdie and C. R. Young, *T.*, 1910, **97**, 1524.

It has long been recognised that the replacement of hydrogen atoms by alkyl groups imposes restrictions on many reactions of derivatives of succinic acid, and this is particularly noticeable in the formation of amides from esters. An extreme case is illustrated by the fact that whereas methyl succinate readily gives an 80 per cent. yield of succinamide, a parallel reaction with methyl *cis*-$\alpha\beta$-dimethylsuccinate proceeds with difficulty, and gives only 2 per cent. of the corresponding amide.[44] It will be seen that this result is in agreement with Fischer's view that the first action of ammonia on an ester is the formation of an unsaturated salt, and lends support to his prediction that a tetramethylsuccinic ester would, in consequence, fail to react with ammonia.

Methylcarbonato-acids.—The methylcarbonato-derivatives of hydroxy-acids are evidently of special value in syntheses where it is necessary to exclude the hydroxyl group from reaction, and several examples of their use in this respect have recently been described. The characterisation of simple types of these compounds is, however, somewhat imperfect, and a detailed account of methylcarbonatoacetic acid will be welcomed.[45] The acid is readily acted on by thionyl chloride to give methylcarbonatoacetyl

[42] C. R. Young, *T.*, 1914, **105**, 1228.

[43] A. Werner and M. Basyrin, *Ber.*, 1913, **46**, 3229; *A.*, 1913, i, 1302.

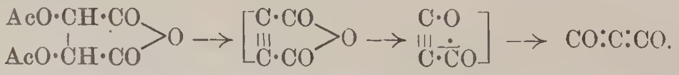
[44] G. F. Morrell, *T.*, 1914, **105**, 2698.

[45] E. Fischer and H. O. L. Fischer, *Ber.*, 1914, **47**, 768; *A.*, i, 381.

chloride (I), from which the corresponding methylanilide (II) is easily obtained:

$$\underset{\text{(I.)}}{COCl{\cdot}CH_2{\cdot}O{\cdot}CO_2Me} \longrightarrow \underset{\text{(II.)}}{NMePh{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}CO_2Me}.$$

As was to be expected, the successive action of sodium hydroxide and hydrochloric acid on the latter compound resulted in the formation of the methylanilide of glycollic acid. In another characteristic change, methylcarbonatoacetyl chloride was brought into reaction with benzene in the presence of aluminium chloride, and, on acidification of the solution, methylcarbonatobenzoylcarbinol, $COPh{\cdot}CH_2{\cdot}O{\cdot}CO_2Me$, was produced. From this, in turn, by the action of alkali, the carbomethoxy-group was expelled, with the formation of benzoylcarbinol. Similar reactions have been carried out on the α-methylcarbonatopropionic acid derived from lactic acid, and consideration of the whole series of changes gives the impression that this new method of temporarily masking the reactive hydroxyl group is extremely important. The use of acetyl derivatives for the purpose mentioned above is less efficacious, as, in addition to the ease with which the substituting groups are removed by hydrolytic reagents, the tendency of these compounds to lose acetic acid is frequently very great. Occasionally this instability leads to interesting results, as, for example, in the conversion of diacetyltartaric anhydride into carbon suboxide.[46] Apparently this reaction involves the elimination of two molecules of acetic acid, thus giving rise to acetylenedicarboxylic anhydride, which, in turn, is converted into carbon suboxide through the intermediate formation of β-oxypropiololactone:



$$\begin{matrix}AcO{\cdot}CH{\cdot}CO\\ |\\ AcO{\cdot}CH{\cdot}CO\end{matrix}\!\!>\!O \longrightarrow \left[\begin{matrix}C{\cdot}CO\\ |||\\ C{\cdot}CO\end{matrix}\!\!>\!O \longrightarrow \begin{matrix}C{\cdot}O\\ |||\;|\\ C{\cdot}CO\end{matrix}\right] \longrightarrow CO{:}C{:}CO.$$

Esters.—As most of the synthetical work involving the use of esters is described under various other headings, there is little necessity to devote a special section to these compounds, particularly as few novel or unusual results have been noted in the period under review. Esters still find manifold applications in condensation reactions, their halogen derivatives are usefully employed in syntheses involving organo-metallic compounds, and, as in the past, they have been the subject of careful physical examination. Attention may be drawn to a study of the hydrolysis of methyl acetate in which hydrogen chloride, in widely varying concentration, was used as a catalyst.[47] In this specific case it has been found that there is no tendency for the temperature-coefficient of a strongly catalysed reaction to be less than that of a weakly catalysed reaction. Evidently, if the effect of a catalyst is merely to increase the ratio of active to unactivated molecules, the temperature coefficient should diminish when the number of active molecules is increased. The results of this investigation certainly lend support to the views expressed by Marcelin that the effect of temperature in accelerating reactions depends on an increase in the internal energy of the reacting molecules, and does not involve any distinction between active and inactive molecules. The theoretical discussion is extended to a consideration of catalysis as a radiation effect, and thus falls within the compass of another section of the Reports.

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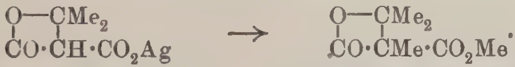
[46] E. Ott, *Ber.*, 1914, **47**, 2388; *A.*, i, 1048.

[47] A. Lamble and W. C. M. Lewis, *T.*, 1914, **105**, 2330.

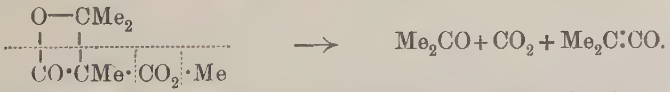
Lactones.—Probably the most comprehensive study of simple lactones which is to be reported is described by Nef in connexion with the examination of acids allied to the sugars. This is, however, dealt with later under carbohydrates, and, in the meantime, attention may be directed to various extensions of earlier work on the reactions of β-lactones.

As a rule, complex changes ensue when a β-lactone is heated, and the formation of ketens in such reactions has been traced in an examination[48] of the decomposition undergone by the esters of certain lactonic acids. By the interaction of methyl iodide and the β-lactone of silver β-hydroxy*iso*propylmalonate, the ester obtained is, curiously enough, not a derivative of the parent acid, but of the β-lactone of β-hydroxy-α-methyl*iso*propylmalonic acid:



$$\begin{array}{l}\text{O—CMe}_2\\ \text{CO}\cdot\text{CH}\cdot\text{CO}_2\text{Ag}\end{array} \longrightarrow \begin{array}{l}\text{O—CMe}_2\\ \text{CO}\cdot\text{CMe}\cdot\text{CO}_2\text{Me}\end{array}.$$

This irregular reaction resembles in many ways the action of alkyl iodides on the silver salts of hydroxy-acids, where, in addition to the normal ester, the corresponding alkyloxy-ester is invariably formed to some extent. The ester formulated above is remarkably stable, but is decomposed when heated in an inert atmosphere to give a notable yield of dimethylketen, together with acetone and carbon dioxide:



$$\begin{array}{l}\text{O—CMe}_2\\ \text{CO}\cdot\text{CMe}\cdot\text{CO}_2\cdot\text{Me}\end{array} \longrightarrow \text{Me}_2\text{CO}+\text{CO}_2+\text{Me}_2\text{C:CO}.$$

The reaction appears to involve molecular rupture in the manner indicated by the dotted lines, followed by the transference of a methyl group to the keten residue, and, although this may appear a somewhat empirical explanation of the change, it is supported by the fact that bromomethylketen, CBrMe:CO, has been obtained in a parallel reaction from the corresponding α-bromo-lactonic ester.

[48] E. Ott, *Annalen*, 1913, **401**, 159; *A.*, 1913, i, 1302.

Aldehydes and Ketones.—The preparation of aldehydes and ketones by methods depending on catalytic agency still continues to be prominent, but there is little under this heading to add to the account given in 1913, except that manganous oxide has been used with considerable success as a catalyst in these reactions.[49] The reagent is claimed to possess several advantages over titanic oxide in this type of reaction, and is possibly more uniform in its effect than thorium oxide, which sometimes gives irregular results.

During the past few years, the preparation and study of unstable aldehydes have been greatly extended, and a new synthetical method for the preparation of certain types of such compounds has to be noted. As is well known, the methods hitherto in use for the preparation of glyoxals are not only experimentally difficult, but are frequently uncertain in their results. The following series of reactions, however, appear to be general in their application, and to proceed smoothly.[50]

Ethyl diethoxyacetate may be condensed with ethyl acetate by the agency of sodium:

$$CH(OEt)_2{\cdot}CO_2Et \longrightarrow CH(OEt)_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et.$$

The product (or its homologues) is then hydrolysed by dilute acids, giving, in the first instance, an acetal, and finally the corresponding alkylglyoxal, $CH(OEt)_2{\cdot}CO{\cdot}R \longrightarrow CHO{\cdot}CO{\cdot}R$. The properties of a number of new glyoxals are now described, and, in future, these compounds will be more readily available. It is significant that most of the new representatives display the yellow-green colour which appears to be characteristic of all true glyoxals. As was to be expected, the compounds are readily converted into the corresponding hydroxy-acids, and it is to be noted that the enzyme, glyoxalase, effects the same change, but gives optically active products. This is an important observation, the significance of which will be obvious.

The preparation of aldehydes by direct oxidation of the corresponding alcohol is generally a difficult operation, and in this connexion it is well to draw attention to a paper in which the preparation of pure glyceraldehyde from glycerol is described.[51] The oxidation was effected by means of Fenton's reagent, and the product, isolated through the intermediate formation of the diethylacetal, was obtained in the crystalline state. These reactions have, of course, already been carried out, but the special feature of the paper, which should be consulted by those who have occasion to employ hydrogen peroxide in similar reactions, is the precise experimental conditions which are established, both for the use of Fenton's reagent and for the production of acetals.

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[49] P. Sabatier and A. Mailhe, *Compt. rend.*, 1914, **158**, 830; *A.*, i, 547.

[50] H. D. Dakin and H. W. Dudley, *T.*, 1914, **105**, 2453.

[51] E. J. Witzemann, *J. Amer. Chem. Soc.*, 1914, **36**, 2223; *A.*, i, 1165.

Polyhydric Alcohols and their Derivatives.

Few methods for effecting the apparently simple change of a dibromo-compound of the type of ethylene dibromide into the corresponding glycol are satisfactory so far as yields are concerned. Even the preliminary conversion of the halogen compounds into acetates is, in many cases, no more effective than the direct process, and unsaturated derivatives of the type of vinyl bromide are frequently formed, according to the scheme

$$CR_2Br\cdot CHRBr \longrightarrow CR_2\colon CRBr.$$

It has been shown in a careful study of this process that the use of silver acetate as a reagent for decomposing dibromides is less open to objection in this respect than is that of potassium acetate.[52] Further, the ease with which diacetates are formed from dibromides is less in higher than in lower homologues, and is diminished when the two bromine atoms are in spatial proximity. This agrees with the experience of other workers who have been engaged on similar topics, and a number of striking experimental facts are recorded by Franke,[53] who has shown that dibromides of the type

$$CH_2Br\cdot CRR'\cdot CH_2Br$$

are notably stable towards both potassium cyanide and silver acetate. On the other hand, the above reagents react readily with dibromides constituted according to the formula

$$CR_2Br\cdot CH_2\cdot CR_2Br,$$

and the suggestion is made that the reaction takes place in two stages, involving: (1) the formation of an unsaturated derivative, and (2) the addition of hydrogen cyanide or acetic acid. Both the papers now quoted may be consulted with advantage by all who are engaged with work involving dibromides, which can only be obtained in small quantity, and the suggestion that sodium ethoxide in dilute alcoholic solution is the most effective reagent for the hydrolysis of diacetates will doubtless find many applications.

Acetylenic glycols offer many possibilities for attractive research, and a representative series of these compounds has been prepared during the past ten years through the agency of magnesium–acetylene derivatives. A simple example may be quoted in illustration of the process.[54] Dimagnesium acetylene dibromide reacts with acetaldehyde to give the additive compound,

$$MgBr\cdot O\cdot CHMe\cdot C\vdots C\cdot CHMe\cdot O\cdot MgBr,$$

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[52] E. G. Bainbridge, *T.*, 1914, **105**, 2291.

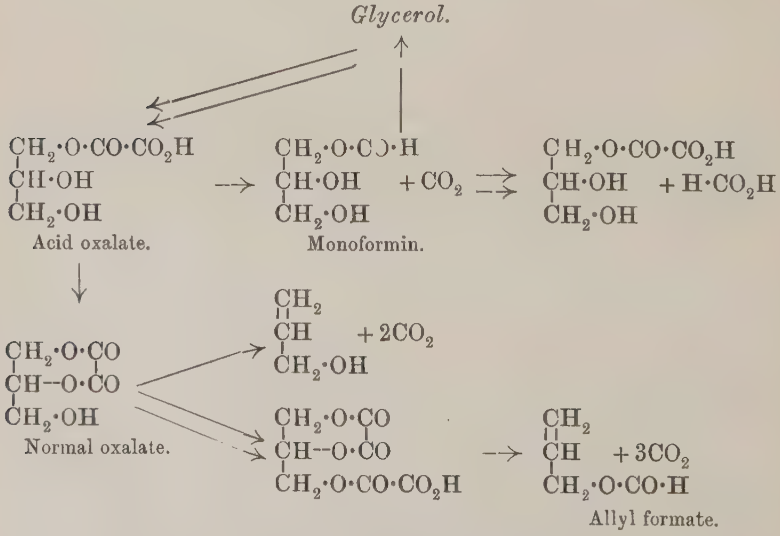
[53] A. Franke, *Monatsh.*, 1913, **34**, 1893; *A.*, i, 7.

[54] S. I. Iocitsch, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 430; *A.*, i, 375.

from which, on decomposition with water, the corresponding unsaturated glycol, OH·CHMe·C⋮C·CHMe·OH, is produced. The reaction, which is applicable to substituted aldehydes and also to aliphatic or cyclic ketones,[55] seems perfectly general, and has been applied to a large number of cases. Now that improved methods for the preparation of unsaturated glycols are available, the examination of these compounds is being carried out in considerable detail.[56]

Glycerol.—When critical research is brought to bear on reactions familiar to the lecture-room or laboratory, the result is frequently to unfold new difficulties and to complicate the task of teacher and student alike. The opposite result, and the reduction of important reactions to simple terms, is thus doubly welcome.

The interaction of glycerol and oxalic acid under varying conditions has now received a new interpretation, which will be generally accepted.[57] Both an acid and a normal oxalate are produced, and the decomposition of these esters gives rise to all the known products of the reaction. In the following structural outline, which illustrates most of the changes involved, the double arrows indicate the stages in which oxalic acid plays a part in the reaction, but the original paper should be consulted for the evidence upon which the scheme is based:



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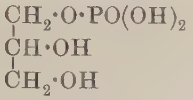
[55] S. I. Iocitsch, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 656 ; *A.*, i, 375.

[56] R. Lespieau, *Compt. rend.*, 1914, **158**, 707 ; *A.*, i, 476 ; G. Dupont, *ibid.*, 714 ; *A.*, i, 530.

[57] F. D. Chattaway, *T.*, 1914, **105**, 151.

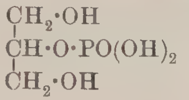
In last year's Report, reference was made to one aspect of the controversy, which has been maintained for many years, as to the nature and constitution of the glycerylphosphates, and the opinion was expressed that the problem should be attacked by entirely different methods. During the current year an important paper[58] has appeared, in which the cognate literature since 1903 is carefully reviewed, and, in addition, the fresh experimental facts recorded have cleared up a number of doubtful points. The simplest possible glycerylphosphoric acid should exist in two forms,



$$\begin{array}{l} CH_2{\cdot}O{\cdot}PO(OH)_2 \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array}$$

(I.)
(α-Form.)

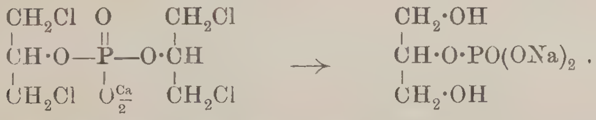
and



$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}O{\cdot}PO(OH)_2 \\ | \\ CH_2{\cdot}OH \end{array}$$

(II.)
(β-Form.)

and only the α-isomeride should be capable of resolution into active modifications. Previous attempts to synthesise the isomerides in a state of purity have only been partly successful, as the tendency of these esters to form polyglyceryl derivatives is very great. Even the identification of the glycerylphosphoric acid obtained by the hydrolysis of lecithin as an active modification corresponding with formula I is still doubtful. It has now been shown that the action of phosphoryl chloride on α-dichlorohydrin is somewhat less complex than was at one time imagined. The product undergoes hydrolysis in two stages, giving, in succession, bis-*s*-dichloro*iso*propylphosphoric acid and β-glycerylphosphoric acid. As calcium hydroxide and sodium carbonate were employed as the hydrolytic agents, the compounds actually isolated had the following structure:



$$\begin{array}{lcl} CH_2Cl \quad O \quad\quad CH_2Cl & & CH_2{\cdot}OH \\ |\qquad\quad \| \qquad\quad | & & | \\ CH{\cdot}O{-}P{-}O{\cdot}CH & \longrightarrow & CH{\cdot}O{\cdot}PO(ONa)_2\,. \\ |\qquad\quad | \qquad\quad | & & | \\ CH_2Cl \quad O\frac{Ca}{2} \quad CH_2Cl & & CH_2{\cdot}OH \end{array}$$

The sodium β-glycerylphosphate proved to be identical with the compound formed by the interaction of monosodium phosphate and two molecules of glycerol, followed by hydrolysis of the resulting diglyceryl ester.

For the preparation of the corresponding α-glycerylphosphoric acid, a new and apparently simpler process was devised in that α-monochlorohydrin was found to react readily with trisodium phosphate, and from the products of this reaction salts of a definite α-glycerylphosphoric acid were obtained:

$$HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl + (NaO)_3PO \longrightarrow$$
$$HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}PO(ONa)_2.$$

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[58] H. King and F. L. Pyman, *T.*, 1914, **105**, 1238.

Those who have worked in this field will realise the experimental difficulties involved, and the advance which has been made, in this characterisation of the simplest types of glycerylphosphates.

As pointed out last year, considerable attention is now being devoted to the study of glycerol derivatives in which the hydroxyl groups are only partly substituted, or are replaced by different acyl residues. Numerous papers have since appeared which point to the continuation of this development, and reference may be made to the attempts, so far unsuccessful, to synthesise optically active glycerides of a special type.[59] A glyceride of the general structure $OR{\cdot}CH_2{\cdot}CH(OR'){\cdot}CH_2{\cdot}OR^2$, where R and R^2 represent different acyl residues and R' may consist of an acyl group or hydrogen, should exist in active forms, the asymmetry being dependent on the glycerol component of the molecule. Compounds of this description should not only be of considerable physiological interest, but might be of service in the study of lipolytic ferments, and thus lead to the identification of the specific enzymes responsible for the degradation of fats in definite stages. Although the research has not, in the meantime, given many positive results, the work has incidentally furnished a description of a number of optically active halogen hydrins. For example, $\beta\gamma$-dibromopropylamine was resolved by *d*-tartaric acid and converted into the corresponding active bromohydrins by the action of nitrous acid. In any circumstances, the replacement of both bromine atoms by acyl groups would not be likely to proceed smoothly, and the ease with which the active bromohydrins are racemised has, so far, limited the development of the research, although the fact that the *d*- and *l*-epibromohydrins seem somewhat more stable leads to the hope that the original object of the work will be achieved.

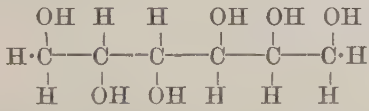
As in the sugar group, the problems affecting the chemistry of fats are now being attacked by two distinct methods. In the one case, ordinary synthetical or analytical reagents are employed, whilst in the other the synthetic or hydrolytic functions of enzymes are brought to bear. In this connexion, many features of primary importance are indicated in the results of experiments in which the synthetic and hydrolytic effects of lipase are compared.[60] Both the rate and extent of the hydrolysis of triolein by means of lipase are retarded as the amount of water present is increased, and the same holds true for the synthesis of the triglyceride. The factors contributing to this result differ, however, according as the change is hydrolytic or synthetic. In the former case, the water prevents contact between the enzyme and the oil, whilst during the synthetic

[59] E. Abderhalden and E. Eichwald, *Ber.*, 1914, **47**, 1856; *A.*, i, 801.

[60] H. E. Armstrong and H. W. Gosney, *Proc. Roy. Soc.*, 1914, [*B*], **88**, 176; *A.*, i, 1149.

reaction the water acts directly by removing glycerol in solution. The important observation is made that not only does the hydrolysis of triolein by lipase proceed in definite stages, giving a di- and mono-glyceride, but that the synthetic action likewise shows a tendency to be arrested at a stage when the diglyceride constitutes the main product.

With the exception of investigations connected with biochemical problems, comparatively few researches have been concerned with polyhydric alcohols higher than glycerol. The detailed chemistry of these compounds is, however, by no means exhausted, and much work remains to be done in this field. Considering the importance of compounds allied to sugars which contain a methyl group in the terminal position of the carbon chain, the synthesis of a methyl tetritol[61] will be recognised as a step in the direction of arriving at the configuration of the methyl tetroses and pentoses. The compound in question was isolated, together with the corresponding aldose, by the reduction of dihydroxyvalerolactone. It may be remarked that although the configuration of active polyhydric alcohols is generally established by their relationship to the sugars, it is possible to obtain the necessary evidence by another method. The condensation of polyhydric alcohols with acetone gives rise to *iso*propylidene derivatives, the stability of which is dependent on the configuration of the hydroxyl groups involved.[62] For example, it is possible by carefully regulated hydrolysis to remove the three acetone residues from tri-*iso*propylidenemannitol in definite stages, and by means of a somewhat complex experimental treatment it is possible to make this result the basis for the allocation to mannitol of the following configuration:



$$\begin{array}{ccccccccccccc} & \mathrm{OH} & & \mathrm{H} & & \mathrm{H} & & \mathrm{OH} & & \mathrm{OH} & & \mathrm{OH} & \\ & | & & | & & | & & | & & | & & | & \\ \mathrm{H}\cdot & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & \cdot\mathrm{H} \\ & | & & | & & | & & | & & | & & | & \\ & \mathrm{H} & & \mathrm{OH} & & \mathrm{OH} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & \end{array}$$

It will be remarked that, in the above structure, definite positions are ascribed to the terminal primary hydroxyl groups, and there seems every reason to believe that the idea is not only justified, but furnishes an explanation for many of the irregular reactions of active alcohols of this type. Thus, to select one illustration, it has been shown that mannitol is only capable of forming penta-ethers,[63] and that it is impossible to extend the alkylation to one of the terminal hydroxyl groups. This pronounced steric hindrance is consistent with the idea that in mannitol there are three hydroxyl groups in close spatial proximity.

[61] R. Gilmour, *T.*, 1914, **105**, 73.

[62] J. C. Irvine and Miss B. M. Paterson, *ibid.*, 898. [63] *Ibid.*, 915.

Carbohydrates.

The progress made during the year in the study of the simpler carbohydrates has, in many respects, been remarkable, and, in all probability, will lead to future developments of the utmost importance. In the course of the past ten years the adoption of the γ-oxidic formula for reducing sugars and their glucosidic derivatives has practically become universal, and there is thus a certain danger that, by blind adherence to its use, restrictions may be placed both on synthetical methods and on legitimate speculations as to structure. This danger may be avoided if sufficient attention is paid to some recent publications.

As is well known, Nef has been engaged for many years in studying the effect of simple oxidising media on carbohydrates, and this inquiry has involved a re-investigation of an old problem—the changes undergone by reducing sugars in the presence of alkalis. Following the usual method adopted by this author, publication has been delayed until the results of several independent investigations were complete, so that it is now possible to view the results as a whole. The method has much to commend it, but leaves the reviewer faced with the difficulty of describing, within a limited compass, a large field of important work and a mass of experimental results. The original paper[64] should therefore be consulted, as it is manifestly impossible to give more than an outline of the research and to indicate its relationship to other work.

When an aqueous solution of a hexose is allowed to remain in contact with dilute alkalis, profound changes ensue, and finally an equilibrium is established between the various enolic forms derivable from the parent sugar. The enolisation, and consequently the number of possible products, is diminished when the concentration of the alkaline hydroxide is reduced, but in its fundamental principles the reaction is general, although complicated by the formation of resins and polysaccharides. The unsaturated molecules which are formed show a tendency to undergo fission at the double bond, so that, taking glucose as a type, the following products result:

From glucose $\alpha\beta$-dienol $\longrightarrow$ formaldehyde and arabinose.
From glucose $\beta\gamma$-dienol $\longrightarrow$ diose and triose.
From glucose $\gamma\delta$-dienol $\longrightarrow$ glyceraldehyde.

The action of mild oxidising agents on mixtures such as that described above results in independent oxidation of the components with the formation of carbon dioxide, formic and oxalic acids, together with a series of hydroxy-acids. The identification of the latter compounds necessitated their separate preparation, the re-determination of their physical constants, and a study of the conditions under which they are converted into lactones. The results are somewhat unexpected. *d*-Mannonic acid, for example, is easily converted into *d*-mannono-*β*-lactone,

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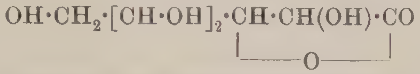
[64] J. U. Nef, *Annalen*, 1914, **403**, 204; *A.*, i, 490.



$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_2{\cdot}\underbrace{CH{\cdot}CH(OH){\cdot}CO}_{O}$$

which rapidly undergoes spontaneous conversion into the parent acid in aqueous solution. The compound thus differs sharply from the corresponding γ-lactone, which is comparatively stable. Similarly, gluconic acid yields both a *β*- and a γ-lactone, and the generalisation is claimed that hydroxy-acids corresponding with the formula $C_nH_{2n}O_{n+1}$ yield both bimolecular α-lactones and unimolecular *β*- and γ-lactones. It may be remarked that the properties of the alkylated mannonic acids lend no support to the idea that α-lactones are readily formed.[65] Thus, of the two substituted mannonic acids indicated below, only that with the constitution expressed by formula I forms a lactone, whilst the remaining isomeride could not be converted into any such derivative:

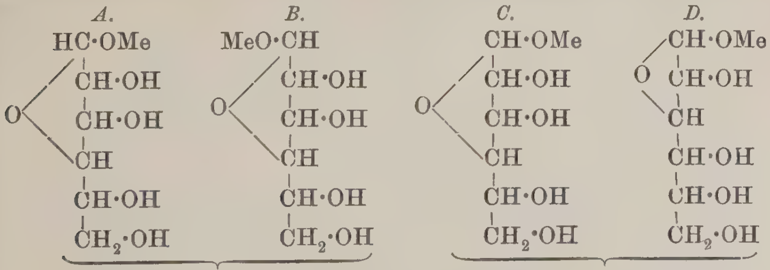
$$OMe{\cdot}CH_2{\cdot}CH(OMe){\cdot}CH(OH){\cdot}[CH{\cdot}OMe]_2{\cdot}CO_2H$$

(I.)

$$OMe{\cdot}CH_2{\cdot}[CH{\cdot}OMe]_3{\cdot}CH(OH){\cdot}CO_2H.$$

(II.)

Although the combined experimental results obtained by Nef are obviously of great importance, some of the theoretical conclusions arrived at seem premature; for example, he puts forward the idea that the α- or *β*-lactone structure may be applied to glucosides, and, although this is quite admissable, it is most unlikely that the isomerism between the two crystalline methylglucosides can be referred to a difference in the mode of linkage of the ring-forming oxygen atom. According to existing views, these glucosides may be represented by the formulæ A and B, shown below, whilst, in Nef's



α-Methyl-glucoside. *β*-Form.

α-Form (stable). *β*-Form (unstable).

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[65] J. C. Irvine and Miss B. M. Paterson, *loc. cit.*

opinion, the isomerism does not depend on the position of the methyl group, but, as indicated in formulæ C and D, on the existence of different ring-structures in the molecule.

These conclusions have been challenged by Fischer,[66] who tabulates powerful arguments in favour of the older formulæ and at the same time describes a new isomeric form of methylglucoside (termed by him "γ-methylglucoside"), which is characterised by the extreme ease with which it is hydrolysed. For this reason formula *D* may possibly be applicable to the new type of glucoside, although the exact linking is still uncertain. It may be remarked that, in addition to the evidence quoted by Fischer, the older formulæ for the alkylglucosides are also supported by recent determinations of their dissociation constants.[67]

The present position of this subject is full of possibilities. Fischer's discovery shows that recognition must now be given to the possible occurrence of a new mode of linking, both in glucosides and in disaccharides. The structure of many important compounds, including the fructosides generally and sucrose in particular, is involved. Although Fischer's results are so far incomplete, they can be verified by the experiences of the writer of this Report, as γ-methylglucoside, in the form of its methylated derivatives, has been recently encountered in attempts to prepare trimethyl glucose from glucosemonoacetone.

Another question involved in this new development is the inadequacy of the existing system of nomenclature to express the structure of sugar derivatives. The expressions α and β, as applied to sugars and glucosides, refer to definite stereoisomeric forms, and their use has become standardised. The same alphabetical system is, however, also used to indicate the consecutive carbon atoms of the sugar chain, and the results described above add considerably to the consequent confusion. Fischer's γ-methylglucoside may be described as an α-, β-, δ-, or ζ-glucoside in that the oxygen atom of the ring may be connected to any one of these carbon atoms of the chain, whilst the compounds generally known as α- and β-methylglucosides may, for similar reasons, be termed γ-methylglucosides. These are by no means the only examples which point to the necessity for radical changes in the present usage.

The fact that the γ-oxidic linking present in one sugar derivative need not of necessity persist during the formation of other derivatives is emphasised by the results lately obtained in connexion with the compound known as glucal. In last year's Report reference was made to the unexpected course followed by the reduction of acetobromoglucose, and it is to be noted that the provisional formula then ascribed to the product has now been modified as the result of further work.[68] The unsaturated and reducing properties of glucal disappear when the compound is reduced catalytically, the change involving the addition of two hydrogen atoms. From this result, and on consideration of the properties of the hydroglucal formed, an alternative structure for glucal has been suggested. This is indicated in the following scheme, which shows the mutual relationship of these interesting compounds with the acetobromoglucose from which they are prepared:

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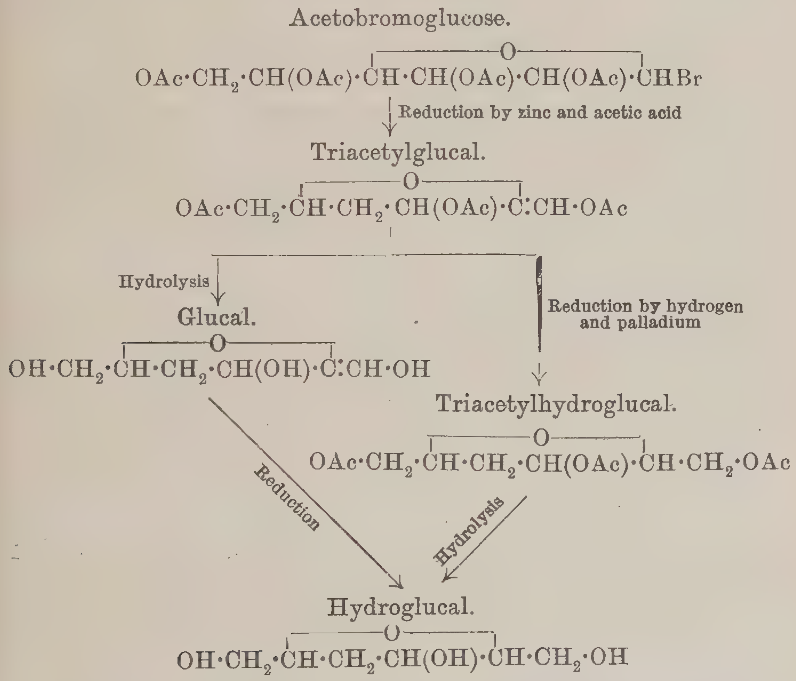
[66] E. Fischer, *Ber.*, 1914, **47**, 1980.

[67] L. Michaelis, *ibid.*, 1913, **46**, 3683; *A.*, i, 16.


Acetobromoglucose.

$OAc\cdot CH_2\cdot CH(OAc)\cdot \overset{\ulcorner\text{———}O\text{———}}{CH\cdot CH(OAc)\cdot CH(OAc)\cdot CHBr}$

Triacetylglucal.

$OAc\cdot CH_2\cdot \overset{\ulcorner\text{———}O\text{———}}{CH\cdot CH_2\cdot CH(OAc)\cdot C}{:}CH\cdot OAc$

Glucal.

$OH\cdot CH_2\cdot \overset{\ulcorner\text{———}O\text{———}}{CH\cdot CH_2\cdot CH(OH)\cdot C}{:}CH\cdot OH$

Triacetylhydroglucal.

$OAc\cdot CH_2\cdot \overset{\ulcorner\text{———}O\text{———}}{CH\cdot CH_2\cdot CH(OAc)\cdot CH}\cdot CH_2\cdot OAc$

Hydroglucal.

$OH\cdot CH_2\cdot \overset{\ulcorner\text{———}O\text{———}}{CH\cdot CH_2\cdot CH(OH)\cdot CH}\cdot CH_2\cdot OH$

Reduction by zinc and acetic acid
Hydrolysis
Reduction by hydrogen and palladium
Reduction
Hydrolysis

These remarkable and unexpected changes, taken in conjunction with Nef's results, will no doubt foster the development of the chemistry of the sugars on less stereotyped lines than has recently been the case. Reactions of the type described above are not confined to glucose alone, but are apparently of general application. Thus, lactose[69] and cellobiose[70] have been respectively converted into lactal and cellobial, which resemble glucal in their essential properties, and undergo similar hydrogenation to give saturated products. It is conceivable that many natural compounds, closely related to the sugars, may possibly be derivatives of the glucals, and the suggestion has already been made[71] that the "carbohydrate" group present in the nucleic acids is in reality related to glucal or an allied compound.

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[68] E. Fischer, *Ber.*, 1914, **47**, 196 ; *A.*, i, 252.

[69] E. Fischer and G. O. Curme, *ibid.*, 2047 ; *A.*, i, 931.

[70] E. Fischer and K. von Fodor, *ibid.*, 2057 ; *A.*, i, 932.

A novel method for the resolution of racemic sugars has also been described, which is based on the formation of active mercaptals by the action of *d*-amyl mercaptan on inactive aldoses.[72] As mercaptals are usually easily purified, the process would appear to be experimentally simpler than the methods which depend on the use of active hydrazine derivatives, but its range of application may be restricted by the fact that the constitution of mercaptals of this nature is quite unknown.

Glucosides.—In last year's Report, attention was directed to recent advances in the synthesis of glucosides by means of enzymes, and, although considerable progress has been made in the period now under review, it is unnecessary to refer again to this line of work in anything like detail. It may be mentioned, however, that in addition to the synthesis of several galactosides and other compounds of simple type, the process of enzyme synthesis has now been successfully applied to the formation of definite monoglucosides of glycol and glycerol.[73] These results are mentioned as they furnish additional evidence that this method of synthesis can be utilised for the preparation of hydroxy-glucosides which are only obtained with exceptional difficulty by ordinary synthetical processes.

The constitution of glucosides and many other structural questions in the sugar group may be solved through the agency of methylation, but work of this nature has, in the past, been somewhat restricted owing to the expense involved in preparing alkylated sugars by the silver oxide method. A considerable simplification has, however, been effected, in that, under carefully controlled conditions, methyl sulphate and sodium hydroxide may be employed for this purpose.[74] In view of the sensibility of many sugars and glucosides to the action of acids or alkalis, the use of these reagents may seem surprising, but the results already available show that the method is general in its application, whilst the fact that octamethyl sucrose can be prepared in quantity by this

[71] R. Feulgen, *Zeitsch. physiol. Chem.*, 1914, **92**, 154; *A.*, i, 1098.

[72] E. Votoček and V. Vesely, *Ber.*, 1914, **47**, 1515; *A.*, i, 664.

[73] E. Bourquelot and M. Bridel, *Compt. rend.*, 1913, **157**, 1024; *A.*, i, 72; *ibid.*, 898; *A.*, i, 499; *ibid.*, 1219; *A.*, i, 662.

[74] W. N. Haworth, *P.*, 1914, **30**, 293; *T.*, 1915, **107**, 8.

process suggests that the structural problems of the di- and polysaccharides may now be investigated with reasonable prospects of success.

There is no diminution in the synthetic applications of acetobromoglucose, and special reference must be made to the new series of purine glucosides,[75] which have been synthesised by means of this popular reagent. The general method of preparation adopted was to employ the various purines in the form of their silver derivatives, and to act on the acetylated glucosides thus produced with ammonia. The compounds isolated are of special interest, particularly in view of the fact that they may, in the future, be condensed with phosphoric acid, and thus give rise to synthetic nucleotides. In subsequent papers [76] the method is shown to be general, both with regard to the nature of the purine and sugar constituents of the glucosides. The outstanding property of these compounds is the ease with which they are hydrolysed into their components, and this instability, which distinguishes purine glucosides from glucosamine derivatives, is doubtless due to the fact that, in the former, nitrogen is directly attached to the carbon atom of the sugar chain which functions in the formation of the reducing group.[77] Evidence is, in fact, accumulating which points to the idea that the great stability which characterises nitrogen derivatives of the nature of glucosamine is due to the formation of ring structures when an amino-group is in spatial proximity to the acidic reducing group. This is emphasised in a publication describing the conversion of glucosamine into mannose,[78] and also receives strong support from other work, where it has been shown that some of the reactions of α-amino-β-hydroxy-compounds can only be explained on the assumption that these substances may behave as cyclic structures.[79]

Another novel series of glucosides has lately been synthesised by the interaction of acetobromoglucose and the silver salts of thiourethanes.[80] The "mustard oil glucosides" obtained after removal of the acyl groups were, on further hydrolysis, converted into thioglucose, which was isolated in the form of the silver derivative. Unfortunately, owing to the somewhat indefinite properties of these compounds, their characterisation is in the meantime incomplete.

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[75] E. Fischer and B. Helferich, *Ber.*, 1914, **47**, 210 ; *A.*, i, 333.

[76] E. Fischer, *ibid.*, 1377 ; *A.*, i, 662 ; E. Fischer and K. von Fodor, *ibid.*, 1058 ; *A.*, i, 741.

[77] J. C. Irvine, R. F. Thomson, and C. S. Garrett, *T.*, 1913, **103**, 238.

[78] J. C. Irvine and A. Hynd, *ibid.*, 1914, **105**, 698.

[79] J. C. Irvine and A. W. Fyfe, *ibid.*, 1642.

[80] W. Schneider, D. Clibben, G. Hüllweck, and W. Steibelt, *Ber.*, 1914, **47**, 1258 ; *A.*, i, 669 ; W. Schneider and D. Clibben, *ibid.*, 2218 ; *A.*, i, 977 ; W. Schneider and F. Wrede, *ibid.*, 2225 ; *A.*, i, 977.

Much patient and useful work continues to be expended on the isolation of natural glucosides, and the number of galactosides recently obtained in this way is striking, although there is still confusion as to whether these compounds represent cleavage products, derived from complexes, or exist in plants or animals in the preformed state.[81] This question has been raised before, and it is evident that, in view of the increasing number of galactose derivatives now being described and of their somewhat unusual properties, the examination of the parent sugar in greater detail is highly desirable. The natural alkaloidal glucosides are also compounds which present many difficulties, and it would appear that the meagre and confusing references to these substances to be found in the literature can be explained by the fact that several different compounds of this type have been described under the general name of "solanine." Some of these compounds are exceedingly complex,[82] and it is therefore important to notice that a simple representative of the class has been isolated from *Solanum angustifolium*.[83] Another interesting observation[84] is the extraction of a dibenzoylglucoxylose from the leaves and stems of *Daviesia latifolia*, as this substance represents an entirely new type of natural compound. The glucoside is hydrolysed by alkalis with extreme ease to give the non-reducing disaccharide, $C_{11}H_{20}O_{10}$, which, in turn, yields both glucose and xylose on complete hydrolysis. The occurrence of two benzoyl groups in a natural compound is most unusual, and further research on the allocation of these substituents to definite positions will be awaited with much interest.

Tannin.—Although comparatively few new experimental results regarding the constitution of tannin have been recently described, it is evident that the views advocated by Fischer are now meeting with general acceptance. In particular, mention may be made of the fact that Nierenstein has now withdrawn his criticisms of Fischer's structure, and brings forward evidence, based on the behaviour of tannin towards yeast, that the glucose residue is an essential and combined constituent of the tannin molecule.[85] The fact that specimens of tannin derived from different sources show varying specific rotations has, in the past, been quoted in support of the idea that glucose is present only as an accidental impurity in tannin. It has, however, now been shown as the result of careful fractional precipitation of commercial tannin that a number of feebly rotatory isòmerides or impurities are present in average specimens.[86] It may be noted in passing that Fischer's views admit not only of the existence of several isomerides, the rotations of which would doubtless lie far apart, but also of the occurrence of partly substituted glucoses in association with tannin.

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[81] O. Rosenheim, *Biochem. J.*, 1913, **7**, 604; *A.*, i, 225; *ibid.*, 1914, **8**, 110, 121; *A.*, i, 706; E. Fischer, *Ber.*, 1914, **47**, 456; *A.*, i, 389.

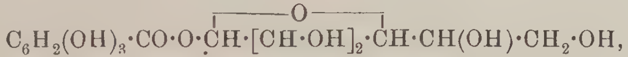
[82] G. Oddo and M. Cesaris, *Gazzetta*, 1914, **44**, ii, 181; *A.*, i, 1173.

[83] F. Tutin and H. W. B. Clewer, *T.*, 1914, **105**, 559.

[84] F. B. Power and A. H. Salway, *ibid.*, 767, 1062.

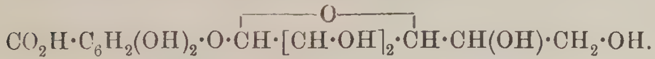
[85] A. Geake and M. Nierenstein, *Ber.*, 1914, **47**, 891; *A.*, i, 567.

Perhaps the most important recent contribution to the tannin problem is a critical examination of the constitution of tannin derived from Turkish and from Chinese galls.[87] It has already been noticed that the glucogallic acid isolated by Feist from Turkish galls is not identical with the β-glucosidogallic acid synthesised from acetobromoglucose. The opinion hazarded in last year's report as to the structural difference between these compounds has now been confirmed, as, on methylation of glucogallic acid, a non-reducing product is obtained, and this, on hydrolysis, yields gallic acid trimethyl ether. The conclusion is drawn that, in the compound under discussion, the glucosidic linking involves the carboxyl group, whereas, in the synthetic isomeride, the coupling of the hexose and aromatic residues involves a phenolic group. This distinction in structure is shown below:



$$C_6H_2(OH)_3\cdot CO\cdot O\cdot \overbrace{CH\cdot[CH\cdot OH]_2\cdot CH}^{O}\cdot CH(OH)\cdot CH_2\cdot OH,$$

(I.) Natural glucogallic "acid."



$$CO_2H\cdot C_6H_2(OH)_2\cdot O\cdot \overbrace{CH\cdot[CH\cdot OH]_2\cdot CH}^{O}\cdot CH(OH)\cdot CH_2\cdot OH.$$

(II.) Fischer's synthetic glucosidogallic acid.

At the same time, although this question of isomerism has probably been definitely settled, the attempts to confirm formula I by synthesis are not convincing. The constitution of the glucogallic acids is, of course, a side-issue of the tannin problem, but the methylation process has also been applied by Feist to the elucidation of the structure of tannins derived from various sources. The principles involved in this method of attack have already been described,[88] and, although scrutiny of the experimental details gives the impression that the methylation was far from being complete, there seems to be no reason why this general method should fail to solve the problem, considering the success which has attended similar attempts to methylate cellulose.

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[86] L. F. Iljin, *Ber.*, 1914, **47**, 985 ; *A.*, 567.

[87] K. Feist and H. Haun, *Arch. Pharm.*, 1913, **251**, 468 ; *A.*, i, 195.

[88] J. C. Irvine, *Biochem. Zeitsch.*, 1909, **22**, 357.

Disaccharides and Polysaccharides.

As usual, the number of papers dealing with the chemistry of disaccharides has been very large, but outside of work the main object of which was obviously technical or analytical there is comparatively little to report.

The debatable question as to whether the inversion of sucrose by invertase is reversible or not has been answered by Hudson in the negative,[89] as in the course of an elaborate investigation, carried out with great care and with the aid of specially active invertase,[90] the results indicate that the hydrolysis of the disaccharide is complete. The synthesis of sucrose by enzyme action is apparently a reaction which has still to be accomplished, in the laboratory at all events, but, on the other hand, evidence has been obtained [91] that dextrorotatory polysaccharides of the nature of glycogen are formed under certain conditions during the alcoholic fermentation of glucose and fructose.

Last year it was noticed that few publications on the complex carbohydrates were available for review, but on this occasion the difficulty has been reversed, as the contributions under this heading have been both numerous and important. Convincing experimental evidence has now been obtained that the action of cold concentrated hydrochloric acid on starch results in rapid degradation, through the usual successive stages, to maltose, the speed of this reaction being much superior to that of the conversion of maltose into glucose. It is shown in the paper now under consideration [92] that the hydrolysis of starch by acids proceeds on essentially similar lines to the action of taka-diastase on the polysaccharide, and that in each of these reactions the glucose finally produced is entirely derived from maltose. In this connexion, reference may be made to an interesting account of the action of taka-diastase on starch, in which the successive formation of $\beta\alpha$-maltose, $\alpha\alpha$-maltose, and glucose is clearly illustrated by graphic methods.[93] Another result, which will not be considered altogether surprising, has been arrived at in the course of these investigations. It is now shown that the action of concentrated hydrochloric acid in effecting the auto-condensation of glucose extends to solutions containing as little as 1 per cent. of the sugar. This observation weakens the conclusions drawn by Willstätter and Zechmeister [94] as to the glucose content of cellulose, but, fortunately, does not seem to affect adversely the attempt to deduce the structure of cellulose by methylation, which was described last year. From the fact that a definite crystalline trimethyl glucose has now been obtained by hydrolysis of methylated cellulose by means of highly concentrated hydrochloric acid, there seems every reason to hope that the linkage of the hexose residues in the polysaccharide will soon be ascertained.[95]

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[89] C. S. Hudson and H. S. Paine, *J. Amer. Chem. Soc.*, 1914, **36**, 1571; *A.*, i, 1148.

[90] C. S. Hudson, *ibid.*, 1566; *A.*, i, 1147.

[91] A. Harden and W. J. Young, *Biochem. J.*, 1913, **7**, 630; *A.*, i, 237.

[92] A. J. Daish, *T.*, 1914, **105**, 2053, 2065.

[93] W. A. Davis, *J. Soc. Dyers*, 1914, **30**, 249.

[94] *Ann. Report*, 1913, 87.

To return to the subject of the diastatic hydrolysis of starch, it must be admitted that the process is, in all probability, much more complex than is generally supposed. There is even considerable doubt in the minds of all who have worked with maltose as to whether a perfectly pure specimen of this sugar has ever been obtained, and the opinion is gaining ground that the substance usually described as maltose is a mixture of closely related compounds. To the evidence already available may be added the observation that, during the action of malt diastase on starch granules,[96] a dextrin is produced the molecular weight of which is nearly equal to that of maltose. Again, many recent experiments[97] go to show that average specimens of starch consist of mixtures of compounds which are practically identical in their properties, and this may serve to explain many of the discordant results to be found in the literature, both with regard to starch and to maltose.

Even granting that maltose is a definite chemical individual, it is doubtful if the structure at present assigned to the compound is correct. Direct experimental methods bearing on this question are difficult to obtain, but reference may be made to a novel attempt to ascertain the structure of maltose, which depends on an application of Nef's work in the sugar group.[98] Curiously enough, the oxidation of maltose by means of alkaline hydrogen peroxide proceeds, to a large extent, without disruption of the disaccharide into glucose. The essential product thus obtained was a glucosidoglycollic acid, which was subsequently hydrolysed into glucose and glycollic acid. So far as these results go, it would appear that Fischer's formula for maltose, if not confirmed, is at least supported.

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[95] W. S. Denham and Miss H. Woodhouse, *T.*, 1914, **105**, 2357.

[96] J. L. Baker and H. F. E. Hulton, *ibid.*, 1529.

[97] C. Tanret, *Compt. rend.*, 1914, **158**, 1353; *A.*, i, 665; *ibid.*, 1914, **159**, 530; *A.*, i, 1167.

[98] W. L. Lewis and S. A. Buckborough, *J. Amer. Chem. Soc.*, 1914, **36**, 2385; *A.*, i, 1199.

Nitrogen Compounds.

Excluding results which are more appropriately discussed under cyclic compounds, or those which bear directly on the problems of physiological chemistry, comparatively few definite advances have been made in the study of aliphatic nitrogen compounds during the past year. Obvious causes have contributed to this fact, but, at the same time, it must be admitted that a certain amount of irregularity and the absence of a definite object characterises much of the synthetical research in this field. Again, as already indicated, the extensive and important work now being carried out in the purine group involves reactions which are characteristic of ring structures rather than of open-chain compounds, so that a comparatively small number of topics are available, on the present occasion, for this section of the Report.

Carbamides.—Considering the present position of our views regarding the mechanism of processes operative in solution, it is not surprising to find that the study of the formation and decomposition of carbamide has again been revived.

In this connexion, it may be noted that the earlier work of Walker and pupils on the change ammonium cyanate ⟶ carbamide has now been completed, so far as the determination of the effect of alcohol on the velocity of the reaction is concerned. Hitherto, on the basis of conductivity measurements, the change has been regarded as dependent on the interaction of $NH_4^{\cdot}$ and CNO' ions, even when 90 per cent. alcohol is used as the solvent, and it is now shown that for alcohol concentrations increasing from 90 to 99·9 per cent. the steady acceleration of the transformation previously observed is maintained. This acceleration holds whether the reaction is referred to the ions of ammonium cyanate or to the non-ionised salt.[99] On the other hand, the addition of alcohol to aqueous or acid solutions of carbamide exerts a marked diminution in the velocity of the decomposition into ammonia and carbon dioxide.[1] This result, although apparently unexpected, certainly supports the idea that the change in question involves the preliminary formation of ammonium cyanate, and is not a simple hydrolysis.

It should be mentioned that the effect of methyl sulphate as a methylating agent has recently been applied successfully to carbamide and its homologues, with the result that methyl ethers of the corresponding *iso*carbamides are formed.[2] Quite apart from the interest attached to this direct formation, from carbamides, of derivatives possessing the *iso*-structure, the reactions of the ethers formed are important from the structural point of view. Thus, when strongly heated, these compounds undergo molecular rupture, the nature of which may be seen from the following representation of the decomposition of *iso*carbamide methyl ether in the form of its methyl hydrogen sulphate:

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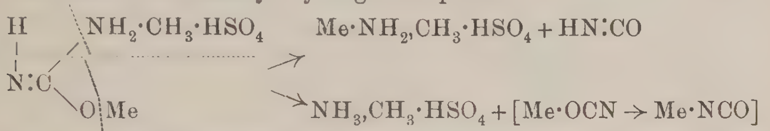
[99] J. D. M. Ross, *T.*, 1914, **105**, 690.

[1] G. J. Burrows and C. E. Fawsitt, *ibid.*, 609.

[2] E. A. Werner, *ibid.*, 923.



This does not exhaust the list of decomposition products, but will indicate the general grounds upon which the idea is based that the constitution of monoalkyl*iso*carbamides is best expressed by the cyclic structure $RN\colon C<^{NH_3}_{O}$, which, in turn, is a reasonable modification of the formula $RN\colon C<^{NH_2}_{OH}$. Compared with carbamide itself, the tendency of thiocarbamide to react in simple changes in accordance with the *iso*-structure is much more pronounced. Several examples may be quoted to illustrate this distinction, and mention may be made of one or two very emphatic cases which have recently come to light. By the action of chloral hydrate on carbamide,[3] direct aldol condensation results, which may involve one or both of the amino-groups, giving the products

$$CCl_3\cdot CH(OH)\cdot NH\cdot CO\cdot NH_2 \text{ and } CCl_3\cdot CH(OH)\cdot NH\cdot CO\cdot NH\cdot CH(OH)\cdot CCl_3.$$

In each case the properties of the products are in agreement with the idea that they are derivatives of normal carbamide, although their behaviour towards acetic anhydride is somewhat irregular.[4] On the other hand, thiocarbamide reacts with chloral hydrate in an entirely different manner, as hydrogen chloride is eliminated during the reaction, with the ultimate formation of

$$NH_2\cdot C(\colon NH)\cdot S\cdot CCl_2\cdot CH(OH)_2.$$

The general nature of this reaction is, therefore, similar to that which ensues when monochloroacetic acid acts on carbamides, as in this case, also, the elements of hydrogen chloride are removed, as shown in the following typical example:[5]

$$NH_2\cdot C(\colon NH)\cdot SH + CH_2Cl\cdot CO_2H = NH_2\cdot C(\colon NH)\cdot S\cdot CH_2\cdot CO_2H + HCl.$$

It would appear, however, from a scrutiny of Feist's work that reactions of the latter type proceed only under the mildest possible conditions, and the complexity of the reactions of thiocarbamides is further emphasised by the behaviour of these compounds towards hypobromites,[6] as in certain cases only one atom of nitrogen is evolved in the reaction, whilst in others both nitrogen atoms are stable. Again, the action of substituted malonic esters on carbamide and thiocarbamide is utterly distinct,[7] although it is to be noted that thiocarbamide reacts with ethyl aminomalonate according to the normal structure to give 2-thiouramil,

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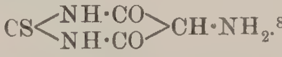
[3] N. G. S. Coppin and A. W. Titherley, *T.*, 1914, **105**, 32.

[4] F. Feist, F. Nissen, and G. Stadler, *Ber.*, 1914, **47**, 1173; *A.*, i, 666.

[5] P. C. Râỳ and F. V. Fernandes, *T.*, 1914, **105**, 2159.



$$CS{<}\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}{>}CH{\cdot}NH_2.$$ [8]

Amino-acids.—A somewhat curious position has arisen in connexion with the chemistry of amino-acids, as the synthesis and decomposition of optically active representatives of this class have practically ceased. As pointed out last year, this is probably largely due to the uncertainty with which all synthetical work of this nature is invested, owing to the occurrence of optical inversion. Work in this field is therefore, in the meantime, largely limited to the identification of naturally occurring amino-acids, the synthesis of simple types, and a study of the general reactions of the compounds without reference to their optical behaviour.

The optical activity of amino-acids is doubtless a complex factor, owing to the tendency of these compounds to form internal salts, and even the rotation of their metallic salts is affected by the fact that they are hydrolysed in aqueous solution.[9] This is shown by the alterations in rotatory power observed when increasing amounts of acid or of alkali are added to solutions of an active amino-acid. In the case of a monobasic acid, the specific rotation undergoes steady alteration until slightly more than the equivalent amount of acid or alkali has been added, after which, on further addition, the optical value remains constant. With dibasic acids, these alterations in rotation are even more instructive, and in such cases, also, constant values are only obtained when the amount of added alkali or acid is slightly in excess of that required for complete neutralisation. In the paper now referred to, the results are extended to a determination of the degree of hydrolysis of salts of amino-acids, and to a calculation of the basic and acidic ionisation constants of the acids examined by this polarimetric method. The results just described do not seem to be affected by the formation in solution of betaine-like salts, but fresh evidence bearing on this point has been obtained in another investigation, which deals with the action of diazomethane on amino-acids and their acetyl derivatives.[10] It appears that the reagent is without action on the free acids, so that, under the conditions of the experiment, a functional carboxyl group is absent. On the other hand, methylation proceeds normally in the case of substituted amino-acids, indicating the presence in these compounds of a normal carboxyl group. The conditions under which α-amino-acids react as cyclic structures are, so far, imperfectly understood, and it is desirable that further research, involving physical methods, should be brought to bear on the subject, as it is no doubt intimately connected with the mechanism of the Walden inversion as experienced with these compounds. The action of nitrous acid on α-amino-acids is, of course, comparatively regular, but is occasionally accompanied by inversion or racemisation, and Fischer has recently encountered another example which emphasises this point.[11] Obviously, the elimination of the amino-group will follow a different course, according as the amino-acid is present in either of the two structural forms shown below:

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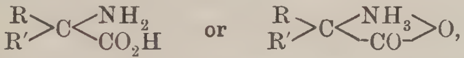
[6] V. von Cordier, *Monatsh.*, 1914, **35**, 9; *A.*, i, 258.

[7] T. B. Johnson and A. J. Hill, *J. Amer. Chem. Soc.*, 1914, **36**, 364; *A.*, i, 330.

[8] T. B. Johnson and B. H. Nicolet, *ibid.*, 355; *A.*, i, 328.

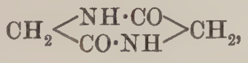
[9] J. K. Wood, *T.*, 1914, **105**, 1988.



$$\genfrac{}{}{0pt}{}{R}{R'}\!>C<\genfrac{}{}{0pt}{}{NH_2}{CO_2H} \quad \text{or} \quad \genfrac{}{}{0pt}{}{R}{R'}\!>C<\genfrac{}{}{0pt}{}{NH_3}{\cdot CO}\!>O,$$

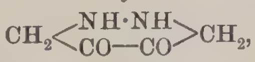
and in optical studies of this change it would be highly desirable to be in possession of an accurate physical method of determining the relative amounts of these isomerides present during the decomposition. It is conceivable that in this way some further generalisations underlying this important change may yet be revealed.

The above structural views may also serve to explain some of the discordant reactions of anhydrides, derived from amino-acids, which have recently been described. For example, the observation that aminoacetaldehyde is produced by the electrolytic reduction of glycine anhydride[12] is not consistent with the normal formula



$$CH_2<\genfrac{}{}{0pt}{}{NH\cdot CO}{CO\cdot NH}>CH_2,$$

as the group $\cdot CO\cdot NH\cdot$ is converted in such reactions into $\cdot CH_2\cdot NH_2$. It has, in fact, been suggested that diketopiperazine is more accurately represented by the formula



$$CH_2<\genfrac{}{}{0pt}{}{NH\cdot NH}{CO—CO}>CH_2,$$

a structure which would easily be derived from the cyclic form of glycine.

JAMES COLQUHOUN IRVINE.

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[10] A. Geake and M. Nierenstein, *Zeitsch. physiol. Chem.*, 1914, **92**, 149 ; *A.*, i, 1057.

[11] E. Fischer and R. von Grävenitz, *Annalen*, 1914, **406**, 1 ; *A.*, i, 1057.

[12] G. W. Heimrod, *Ber.*, 1914, **47**, 338 ; *A.*, i, 327.

PART II.—HOMOCYCLIC DIVISION.

IN spite of the decrease in the output of literature during the last three months of the period under review, the earlier portion of the year showed no falling off in the number of papers dealing with this branch of Organic Chemistry. It will be observed that no writer of the reports on this division of the Science, since their inception, has failed to remark on the difficulties of the task of selection with which he was confronted, and has offered apologies for his many omissions. Indeed, no report could do justice to the mass of material which did not reproduce, in their entirety, the abstracts published in the Journal. To compress into a few pages a review of these numerous researches, when none of them can be described as brilliant and most of them are good, necessitates a selection which, in the nature of things, must be largely haphazard. The writer has therefore selected those communications which seemed to him to be the more important, but he is fully conscious of the fact that he has neglected much that is of value.

One of the most striking features of the literature under review is the large proportion which is devoted to the mere statement of fact, and the small amount which deals with the principles underlying these facts. This condition is, of course, a natural outcome of the great increase in the quantity of literature published during past years, which, becoming an intolerable burden on the financial resources of the publishing societies, has necessitated the shortening of papers, sometimes to such a degree as to render them hardly intelligible. In any case, the discussion of the results of other workers, unless concrete facts are disputed, is either reduced to a minimum or entirely ignored. This is particularly noticeable in international work, and one could easily believe that, in certain countries, no notice whatever is taken of papers published abroad were it not for the fact that internal evidence to the contrary is often forthcoming.

Another disquieting feature is the increasing number of statements which, on subsequent investigation, have proved to be wrong. Many of these, no doubt, are due to clerical errors, but no one who is conversant with the literature of modern organic chemistry can have failed to meet with cases which can only be ascribed to other causes.

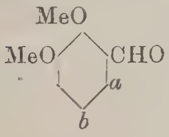
In the ensuing report, the various data have been collected, so far as possible, under general headings.

Nitration.

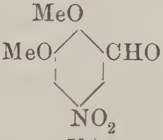
In view of the importance attaching to trinitrotoluene (T.N.T.) at the present time, a communication by W. Will[1] is of interest. Of the six possible trinitro-derivatives of toluene, only three are known, namely, the pure commercial article, the so-called α-trinitrotoluene (m. p. 80·6°), which is 2:4:6-trinitrotoluene; γ-trinitrotoluene (m. p. 104°), obtained from *m*-nitrotoluene, which is 2:4:5-trinitrotoluene; and the β-isomeride (m. p. 112°), formed by the nitration of both 2:3-dinitrotoluene and 3:4-dinitrotoluene, which is 2:3:4-trinitrotoluene. The three isomerides are practically of the same value as explosives.

A search for higher nitrated derivatives proved unsuccessful, because if the reaction is promoted by heat or pressure, either trinitrobenzoic acid, or even tetranitromethane, is obtained. It is pointed out that the intense colour of the latter substance is sometimes noticed in the factory, but that trinitrobenzoic acid, owing to the solubility of its salts, has hitherto escaped detection; its presence is likely to be a source of danger. The author has extended his researches to benzene, and considers that it is extremely doubtful whether a higher nitrated derivative than trinitrobenzene exists.

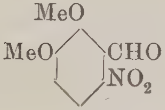
An interesting example of the failure of the aldehyde group to exert its usual directive influence into the meta-position is described by W. H. Perkin and R. Robinson[2] in the nitration of *o*-veratraldehyde. The formula of the aldehyde (I) shows the positions *a* and *b* to be symmetrically placed as regards the methoxy-groups:



(I.)



(II.)



(III.)

It might reasonably be expected, therefore, that the *m*-nitro-derivative (II) would be formed on nitration, whereas the sole product is the *o*-nitro-derivative (III).

A method for preparing nitro-compounds from amino-compounds by the spontaneous decomposition of the nitrites of the corresponding diazo-compounds is described by W. Körner and A. Contardi.[3] The process appears to be of some value, since, for example, 2:6-dibromosulphanilic acid can be quantitatively converted by this means into 2 : 6-dibromonitrobenzene-4-sulphonic acid, and two substituted dinitrobenzenes can also be prepared from the corresponding nitroanilines.

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[1] *Ber.*, 1914, **47**, 704; *A.*, i, 509.

[2] *T.*, 1914, **105**, 2376.

[3] *Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 625; *A.*, i, 263.

The bromine-titration method, applied with success to ethyl acetoacetate and similar substances, has been extended to an investigation of the desmotropism exhibited by nitro-compounds and nitroketones.[4] There appears to be a fundamental difference between the phenomenon as shown by this type and that exhibited by the keto-enol compounds. Thus, whereas the enolic form of, for example, ethyl acetoacetate is favoured least by water, more by methyl alcohol, and still more by ethyl alcohol, the reverse is the case with the *iso*nitro-compounds. This observation is in accordance with the rule that the proportions of the two isomerides depend on their solubilities in the solvent, for enols are less soluble than ketones in water, but *aci*-compounds are more soluble than true nitro-compounds.

Azo-compounds.

K. H. Meyer and S. Lenhardt[5] have already proved that, contrary to the usually accepted idea, not only phenols, but phenolic ethers, couple with diazonium salts to form azo-compounds. Investigation now shows[6] that, speaking generally, the introduction of negative groups into the diazonium salts increases their activity towards coupling with phenolic ethers. Thus the diazonium salt derived from 2 : 4-dinitroaniline couples readily with anisole and with phenetole, and combines immediately with the ethers of resorcinol and α-naphthol. On the other hand, the introduction of negative groups into the phenolic ethers diminishes their tendency to couple, whilst positive radicles, especially alkyloxy- and alkyl groups in the meta-position, increase the tendency to form azo-compounds.

K. v. Auwers and F. Michaelis[7] confirm the latter statement, but point out that a free para-position is essential, and that the speed of the reaction is increased when there is a second alkyl group in the ortho-position, and is at its maximum when the two alkyl groups are both meta to the ether group.

There is a great deal to be said for the view advanced by K. H. Meyer[6] and his co-workers to the effect that this coupling represents an addition of the diazo-salt to a double bond of the second component. They point out that the methyl ether of 9-methylanthranol, which possesses no "active" hydrogen atom in the ortho- or para-positions, can nevertheless couple with *p*-nitrobenzenediazonium hydroxide, in accordance with the scheme:

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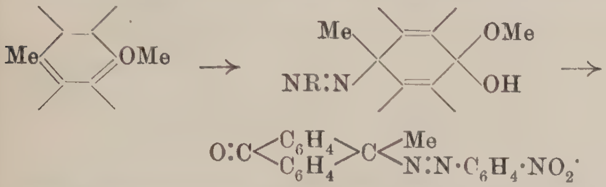
[4] K. H. Meyer and P. Wertheimer, *Ber.*, 1914, **47**, 2374 ; *A.*, i, 1061.

[5] *Annalen*, 1913, **398**, 66 ; *A.*, 1913, i, 723.

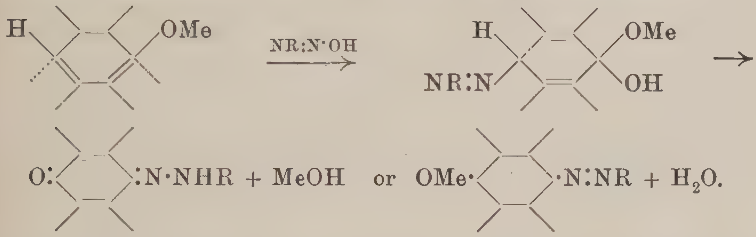
[6] K. H. Meyer, A. Irschick, and H. Schlösser, *Ber.*, 1914, **47**, 1741 ; *A.*, i, 882.

[7] *Ber.*, 1914, **47**, 1275 ; *A.*, i, 744.



$$O{:}C\!<\!\begin{smallmatrix}C_6H_4\\ C_6H_4\end{smallmatrix}\!>\!C\!<\!\begin{smallmatrix}Me\\ N{:}N\cdot C_6H_4\cdot NO_2\end{smallmatrix}.$$

They therefore regard the coupling of a diazonium salt with a phenolic ether as taking place in the following manner:



This explanation also accounts for the fact that, in some cases, the coupling of the diazo-compound and the alkyloxy-compound yields a large proportion of the free hydroxyazo-derivative.

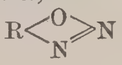
The supposed isomeride of azobenzene obtained by C. V. and R. A. Gortner,[8] which melted at 25°, and was found to be convertible into ordinary azobenzene (m. p. 68°) by means of dilute hydrochloric acid, has been investigated by H. B. Hartley and J. M. Stuart,[9] and is found to be a solid solution of azobenzene in azoxybenzene.

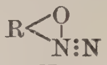
It is well known that phenol and *o*- and *m*-cresol form bisazo-compounds in concentrated, but not in dilute, solutions; thymol and carvacrol also react in the same way. It is now pointed out[7] that the tendency to the formation of bisazo-compounds rises with the number of alkyl groups in the phenol molecule, whereas the presence of other substituents, such as the nitro-, carboxyl, and carboxylic ester groups, destroys, not merely the tendency to, but frequently the possibility of, such condensation. It is also stated that, as a general rule, negative substituents diminish the reactivity of the phenol and that the formation of the bisazo-compound is controlled not so much by the speed of coupling of the phenol as of the monoazo-compound. Bisazo-compounds are best formed in alkali hydroxide solutions, not so well in the presence of alkali carbonates, and scarcely at all in acetic acid.

[8] *J. Amer. Chem. Soc.*, 1910, **32**, 1294; *A.*, 1910, i, 790.

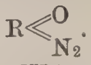
[9] *T.*, 1914, **105**, 309.

The so-called diazophenols can be represented by three constitutional formulæ,


(I.)


$R<^{O}_{N:N}$

(II.)


$R \lessdot ^{O}_{N_2}$.

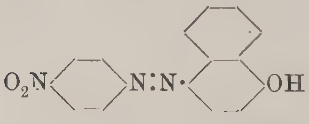
(III.)

Wolff's researches have rendered formula I improbable, and he, with Hantzsch, favours the third constitutional formula. A. Klemenc[10] now brings forward evidence in favour of formula II. He argues that whilst the explosive character of these compounds agrees with either constitution, the fact that the substances dissolve in concentrated acids and can be recovered on dilution would suggest that they cannot be quinone-diazides of formula III. It seems highly improbable that any definite chemical evidence will ever be obtained which will differentiate between compounds of formulæ II and III, although it is to be remembered that, as the Blomstrand diazonium formula is at present fashionable, it appears reasonable to assign formula II to the diazophenols, since they have many characteristics in common with the diazonium salts.

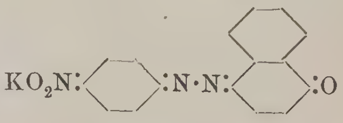
Colour and Constitution.

As the result of the comparison of a large number of colouring matters, a theory is advanced,[11] by which it is stated that those dyes which are quinonoid in all possible tautomeric forms exhibit a deep colour, whereas those which can be represented by formulæ not containing the quinonoid structure are paler in shade. Although this working hypothesis is amply supported by the facts advanced, yet it is evident that the generalisation fails to account for many changes in the intensity of colour which are met with in compounds of closely similar structure and molecular weight. One instance of this kind may be mentioned, namely, the occurrence of blue colours by the coupling of naphthol derivatives with diamino-bases which yield substantive cotton dyes, whilst the same second component yields red colouring matters with those diamino-bases, of closely related structure, which do not produce substantive cotton colours.

The suggestion originally made by J. T. Hewitt and A. D. Mitchell[12] that substances of the type of *p*-nitrobenzeneazo-α-naphthol and its potassium salt have structures represented by the formulæ



and



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[10] *Ber.*, 1914 **47**, 1407 ; *A.*, i, 743.

[11] E. R. Watson, *T.*, 1914, **105**, 759.

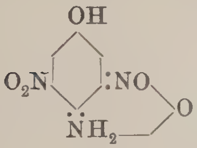
[12] *T.*, 1906, **89**, 19 ; *ibid.*, 1907, **91**, 1251.

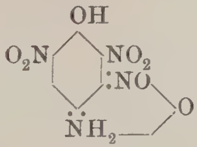
has received support by an extension of the work[13] to *p*-aminoacetophenone and *p*-aminobenzophenone in combination with phenol, *o*-cresol, and *α*- and *β*-naphthol. The results are in accordance with the view that these compounds and their salts should be represented by type A, whereas the corresponding phenylhydrazones are to be expressed by type B:

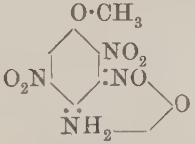
$$\text{A.} \begin{cases} CH_3\cdot CO\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OH. \\ CH_3\cdot C(OK){:}C_6H_4{:}N\cdot N{:}C_6H_4{:}O. \end{cases}$$

$$\text{B.} \begin{cases} CH_3\cdot C({:}N\cdot NH\cdot C_6H_5)\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OH. \\ CH_3\cdot C({:}N\cdot NH\cdot C_6H_5)\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OK. \end{cases}$$

The large amount of work on the nitroaminophenols which has been carried out by R. Meldola and his collaborators for many years past has led to the important conclusion[14] that the condition essential to the production of deep colour is the ortho-position of a nitro-group with respect to an amino- or substituted amino-group. The presence of additional nitro-groups in the nucleus has generally the effect of increasing the intensity of the colour. It is evident that the appearance of colour in these cases cannot be due to the mere presence of nitro- and amino-groups in the nucleus, but must be caused by some more profound change in structure. The compounds named are therefore given the structures indicated by the numbered formulæ: 3:5-dinitro-*p*-aminophenol (I), 2:3:6-trinitro-*p*-aminophenol (II), and 2:3:5-trinitro-*p*-anisidine (III):


(I.)
(Red.)


(II.)
(Red.)


(III.)
(Red.)

An important illustration of the property of colour in relation to tautomerism is brought forward by R. Meldola and W. F. Hollely[15] in connexion with the compound formed by the interaction of 2:3:5-trinitroaceto-*p*-anisidide and aniline. The free compound can be obtained in pale, ochreous needles (IV) or deep red scales (V), the two forms being interconvertible. Both modifications dissolve in alkali, forming a deep orange solution of compound VI:

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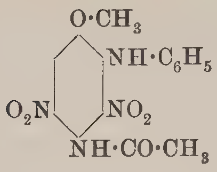
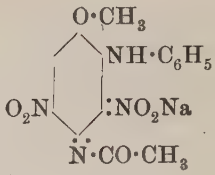
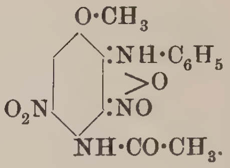
[13] J. T. Hewitt, Miss G. R. Mann, and F. G. Pope, *T.*, 1914, **105**, 2193.

[14] R. Meldola and W. F. Hollely, *ibid.*, 414.

[15] *Ibid.*, 977.


(IV.)


(VI.)


(V.)

Friedel and Crafts' Reaction.

In the last volume of these Reports[16] attention was drawn to the large amount of work which has been published recently on the various applications of this reaction, and at the same time a valuable summary was given respecting our knowledge of the mechanism of the process. During the period under review, several papers have appeared which have an important bearing on this question. S. C. J. Olivier[17] has conducted certain dynamic researches on the course of the reaction, *p*-bromobenzenesulphonyl chloride being used, since it not only reacts with measurable velocity, but is not decomposed by water at the ordinary temperature. Evidence was obtained of the formation of the additive product showing that, partly at any rate, the reaction proceeds in accordance with the scheme:

$$C_6H_4Br{\cdot}SO_2Cl,AlCl_3 + C_6H_6 \longrightarrow C_6H_4Br{\cdot}SO_2{\cdot}AlCl_2 + C_6H_5Cl + HCl.$$

The following conclusions were drawn:

(1) The acid chloride reacts solely in the form of the compound $C_6H_4Br{\cdot}SO_2Cl,AlCl_3$.

(2) One molecule of aluminium chloride cannot transform more than one molecule of acid chloride.

(3) The reaction is unimolecular with respect to the compound $C_6H_4Br{\cdot}SO_2Cl,AlCl_3$.

(4) The reaction constant (when an excess of aluminium chloride is not used, and if K is calculated for the compound $C_6H_4Br{\cdot}SO_2Cl,AlCl_3$) is proportional to the concentration of the aluminium chloride.

(5) The constant is greatly increased by an excess of aluminium chloride.

These facts are most readily explained on the assumption that the acid chloride is activated proportionally to the concentration of the combined aluminium chloride. When benzene is replaced by its derivatives, reaction occurs with diminishing rapidity in the order benzene, bromobenzene, chlorobenzene. No reaction was observed with nitrobenzene. It should be added that the above conclusions receive support from the observation of C. R. Rubidge and N. C. Qua,[18] who find that, in the reaction between benzoyl chloride and benzene in the presence of aluminium chloride, the yield is considerably diminished if the amount of aluminium chloride is reduced.

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[16] *Ann. Report*, 1913, 97.

[17] *Rec. trav. chim.*, 1914, **33**, 91; *A.*, i, 818.

On the other hand, B. N. Menschutkin[19] has continued his experiments on the influence of antimony trichloride and antimony tribromide on condensations of the Friedel and Craft type. The first phase in the reaction involves the formation of a compound of the antimony salt with the hydrocarbon, $2SbCl_3,C_6H_5R$. This compound is then acted on by, for example, benzoyl chloride, yielding a compound of antimony chloride with the ketone, $SbCl_3,C_6H_5{\cdot}CO{\cdot}C_6H_4R$, which decomposes into its constituents at the temperature of the experiment. The antimony trichloride thus liberated may then react with fresh quantities of hydrocarbon and benzoyl chloride. The total reaction, expressed by the equation

$$ArH + C_6H_5{\cdot}COCl + SbCl_3 = Ar{\cdot}CO{\cdot}C_6H_5 + HCl + SbCl_3,$$

proceeds to an end, and gives results in accordance with a bimolecular reaction, the hydrocarbon and benzoyl chloride being taken always in molecular proportions. The velocity of the reaction varies directly as the square of the concentration of the antimony trichloride.

It is certainly difficult to bring the results of these two investigations into line, and it is evident that the problem of the mechanism of this reaction is still unsolved. It should be added that J. Böeseken and M. C. Bastet[20] bring forward further evidence in support of their view that the Friedel and Craft reaction takes place when three molecules are present, the first of which is unsaturated, the second of which can be activated to such an extent that it is decomposed during the reaction into two parts, which then unite with the first molecule, and the third of which can activate the two molecules. The authors describe a series of condensations between benzene and various chloro-derivatives of ethylene in which, in the first stage, the molecule of benzene is disrupted, and then forms a compound with the unsaturated molecule; the latter molecule then becomes disrupted in its turn, and combines with a second or third molecule of benzene, which now behaves as if it were unsaturated.

It has been shown[21] also that aluminium chloride may be used as a means of effecting the elimination of water in certain types of condensation. Thus hydrocarbons of the aliphatic, benzene, naphthalene, and anthracene series have been condensed, not only with chloral, but also with chloral hydrate and bromal, the reactions, which are carried out at 0°, being represented by the equation

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[18] *J. Amer. Chem. Soc.*, 1914, **36**, 732 ; *A.*, i, 539.

[19] *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1710 ; 1914, **46**, 259 ; *A.*, i, 188, 673.

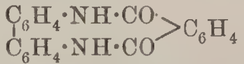
[20] *Rec. trav. chim.*, 1913, **32**, 184 ; *A.*, i, 156.

[21] G. B. Frankforter and W. Kritchevsky, *J. Amer. Chem. Soc.*, 1914, **36**, 1511 ; *A.*, i, 1059.

$$2RH + CCl_3{\cdot}CHO = CHR_2{\cdot}CCl_3 + H_2O.$$

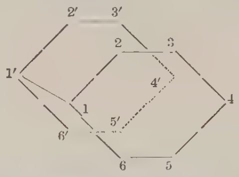
Diphenyl Series.

The stereochemical formula for diphenyl originally proposed by Kaufler[22] to account for the production of cyclic compounds of the type of phthalylbenzidine,



$$\begin{array}{l} C_6H_4{\cdot}NH{\cdot}CO \\ | \\ C_6H_4{\cdot}NH{\cdot}CO \end{array}\!\!>C_6H_4$$

has apparently received support by recent investigations in the diphenyl series.[23] J. C. Cain, A. Coulthard, and Miss F. M. G. Micklethwait[24] have shown already that two distinct *o*-dinitrobenzidines exist, and the cause of this isomerism becomes apparent if it is assumed that in the Kaufler formula,



there is no free rotation between the two benzene rings. The two dinitro-derivatives are therefore 3 : 3′- and 3 : 5′-dinitrodiphenyl. An extension of the work to *o*-tolidine[25] has led to the isolation of two dinitro-*o*-tolidines, and in this instance it was found possible to convert one of them into the other.

Considerable interest attaches to the fact that the four possible*

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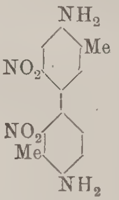
[22] *Annalen*, 1907, **351**, 151 ; *Ber.*, 1907, **40**, 3250 ; *A.*, 1907, i, 794.

[23] J. C. Cain and Miss F. M. G. Micklethwait, *T.*, 1914, **105**, 1438.

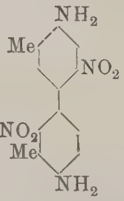
[24] *T.*, 1912, **101**, 2298.

[25] J. C. Cain and Miss F. M. G. Micklethwait, *ibid.*, 1914, **105**, 1442.

* The writer is under the impression that there are six possible isomerides and that the two formulæ

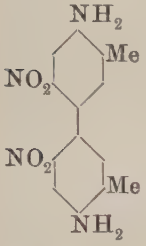


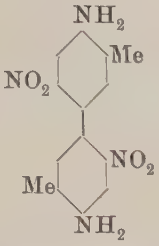
and

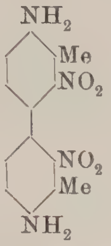


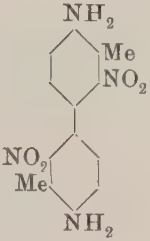
should be included. These compounds contain, however, two dissimilar benzene rings and the argument is not affected by their exclusion.

m-dinitro-derivatives of *o*-tolidine required by the Kaufler formula have been isolated, namely,

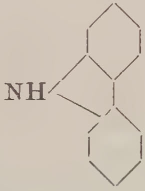




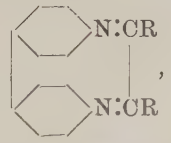




and it is certainly remarkable that no less than three of these give distinct carbazoles on reduction. This involves, in at least one case, the production of *trans*-linking, thus:



Such linking is, of course, known, since the *trans*-forms of many dialkylsuccinic acids, compounds in which the ring-forming elements are separated in the same manner as in these reduced nitro-compounds, yield their own anhydrides, but if this is the case the *trans*-carbazole should be readily convertible into its *cis*-isomeride, which must be identical with one of those derived from the other two bases. It is to be noticed, moreover, that Cain and Miss Micklethwait[26] prepared condensation products of benzidine with *o*-diketones to which they assign the formula:



an assumption which, if correct, would give strong support to the Kaufler formula. J. Kenner and Miss A. M. Mathews[27] point out, however, that in no case was it found possible to free these condensation products from the two molecules of alcohol or other solvent which always accompany them, and they remark that Täuber[28] does not appear to have experienced any difficulty in obtaining similar free condensation products from 2:2′-diaminodiphenyl. They also argue[29] that if Cain and Miss Micklethwait's view as to the isomerism of the two dinitrobenzidines is correct, it is to be anticipated that the prevention of rotation of the two benzene nuclei would also be exhibited in 2 : 2′-diphenyldiacetic acid. Such is, however, not the case, since whilst diethyl diphenyldiacetate furnishes ethyl dibenzo*cyclo*heptadienecarboxylate,[30] diphenyldiacetyl chloride can be converted into hydroxypyrene (II)[31]:

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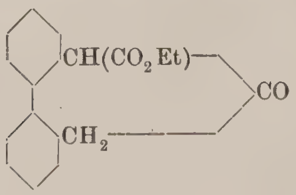
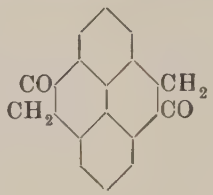
[26] *Loc. cit.*, p. 1440.

[27] *T.*, 1914, **105**, 2473.

[28] *Ber.*, 1892, **25**, 3287; 1893, **26**, 1703; *A.*, 1893, i, 96, 588.



(I.)



(II.)

This argument is, of course, by no means conclusive, since it is conceivable that the reagents used might have caused rotation; moreover, it must be remembered that Cain and Miss Micklethwait[32] prepared a condensation product from tolidine and glyoxal which, although not crystalline, gave a nitrogen content corresponding with that required by the free condensation product. Further work on this subject will be awaited with interest, because it is apparent that more evidence is desirable before the Kaufler formula can be accepted.

Triarylmethyls.

An admirable address on the triarylmethyls has appeared,[33] in which the arguments for and against the conception of free radicles are discussed, and in this connexion certain experiments described by W. Schlenk and E. Marcus[34] are of importance. These investigators find that metals such as sodium or potassium will combine with the free organic radicles if the reaction is carried out in ether solution in an atmosphere of nitrogen. Of the triarylmethyls, only triphenylmethyl presented difficulties, which were, however, overcome, and sodium triphenylmethyl, CPh_3Na, was obtained as a brick-red mass very sensitive to air. The structure of this substance follows from the formation of triphenylmethane by the action of water or hydrochloric acid, and of triphenylacetic acid by the action of carbon dioxide. Methyl iodide and benzyl chloride react at once, forming triphenylethane and *as*-tetraphenylethane respectively.

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[29] *Loc. cit.*, p. 2474.

[30] J. Kenner, *T.*, 1913, **103**, 615.

[31] R. Weitzenböck, *Monatsh.*, 1913, **34**, 199 ; *A.*, 1913, i, 259.

[32] *Loc. cit.*, p. 1441.

[33] M. Gomberg, *J. Amer. Chem. Soc.*, 1914, **36**, 1144 ; *A.*, i, 823.

[34] *Ber.*, 1914, **47**, 1664 ; *A.*, i, 843.

The Cinnamic Acids.

The explanation advanced by E. Biilmann[35] to account for the occurrence of three modifications of *cis*-cinnamic acid, namely, that the acid is trimorphous and can be isolated as *allo*cinnamic acid (m. p. 68°), *iso*cinnamic acid (m. p. 58°), and *iso*cinnamic acid (m. p. 42°), is at the present time very widely held. H. Stobbe and C. Schönburg[36] have now conducted a large number of experiments on the structure of these three acids, and have come to the conclusion that they are, in reality, chemical isomerides. The general impression produced by the paper is that the experiments described can, for the most part, be explained on the Biilmann hypothesis. It would appear desirable, before reopening this question, to frame some really adequate theory to account for more than two stereoisomeric forms of cinnamic acid.

Condensation.

Many papers have appeared during the period under review in which the formation of various types of condensation products is described, but they deal, for the most part, merely with applications of old methods to new conditions. Some, nevertheless, mark a distinct step in advance; thus it has been found[37] that many acid chlorides condense with diphenylketen at the ethylenic linking, forming condensation products, of which diphenylmalonyl chloride, $COCl\cdot CPh_2\cdot COCl$, formed from diphenylketen and oxalyl chloride, may be taken as a type. The reaction does not appear, however, to have a very extended application, since only few acid chlorides react without yielding secondary products of indefinite structure.

The large number of compounds which are at present known having one or other of the alkali metals directly combined with carbon, and which are therefore of considerable importance in synthetic work, has been increased by the extension of the work of W. Schlenk and his collaborators on the formation of the metallic ketyls[38] to a study of the conditions favouring the addition of the alkali metals to compounds containing the complexes C⁚C, C⁚N, and N⁚N.[39] The reactions are carried out in ether solution,

[35] *Ber.*, 1909, **42**, 182, 1443; 1910, **43**, 568; *A.*, 1909, i, 155, 382; 1910, i, 346.

[36] *Annalen*, 1913, **402**, 187; *A.*, i, 173.

[37] H. Staudinger, O. Göhring, and M. R. Schöller, *Ber.*, 1914, **47**, 40; *A.*, i, 285.

[38] W. Schlenk and A. Thal, *A.*, 1913, i, 1205.

[39] W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, 1914, **47**, 473; *A.*, i 396.

and appear to have a general application; thus, the C⁚C compound, stilbene, forms the disodium derivative $CHPhNa\cdot CHPhNa$, the structure of which is proved by the production of *s*-diphenylethane by the action of water, and of the sodium salt of *s*-diphenylsuccinic acid when it is treated with carbon dioxide. The C⁚N compound, benzylideneaniline, yields the disodium salt,

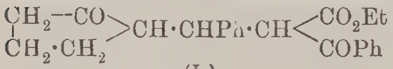
$$NPhNa\cdot CHPh\cdot CHPh\cdot NPhNa,$$

which with carbon dioxide gives the sodium salt of the acid,

$$CO_2H\cdot NPh\cdot CHPh\cdot CHPh\cdot NPh\cdot CO_2H.$$

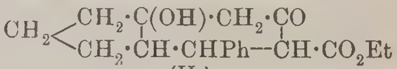
As a type of N⁚N compound, azobenzene was chosen, and in this case an equimolecular mixture of azobenzene and the dipotassium derivative, $NPhK\cdot NPhK$, was formed, from which the potassium salt, $CO_2K\cdot NPh\cdot NPh\cdot CO_2K$, was produced by the action of carbon dioxide.

The work initiated by H. Stobbe on the condensation of cyclic ketones with αβ-unsaturated ketones has been extended[40] to include the condensation of *cyclo*pentanone and 3-methyl*cyclo*hexanone with the ethyl esters of α-benzylidenebenzoylacetic acid and α-benzylideneacetoacetic acid. In the case of 3-methyl*cyclo*hexanone, no condensation could be effected, but *cyclo*pentanone combines with ethyl α-benzylidenebenzoylacetate in the normal manner, yielding the compound I, whereas the condensation between the ketone and ethyl α-benzylideneacetoacetate yields a compound which is thought to be the bicyclic ketone, II:



$$\left.\begin{array}{l}CH_2-CO\\ CH_2\cdot CH_2\end{array}\right\rangle CH\cdot CHPh\cdot CH\left\langle\begin{array}{l}CO_2Et\\ COPh\end{array}\right.$$

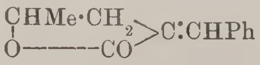
(I.)



$$CH_2\left\langle\begin{array}{l}CH_2\cdot C(OH)\cdot CH_2\cdot CO\\ CH_2\cdot CH\cdot CHPh-CH\cdot CO_2Et\end{array}\right.$$

(II.)

An interesting condensation is described by M. Losanitsch,[41] in which aldehydes and ketones are caused to combine with saturated lactones. The condensations are effected in ethereal solution in the presence of alcohol-free sodium ethoxide, and may be illustrated by the formation of α-benzylidenevalerolactone,



$$\left.\begin{array}{l}CHMe\cdot CH_2\\ O------CO\end{array}\right\rangle C{:}CHPh$$

from benzaldehyde and valerolactone.

The Grignard Reaction.—The question as to the possibility of more than one halogen atom, contained in the molecule of a reacting substance, of combining with the Grignard reagents, has been investigated by E. Votoček and J. Köhler,[42] who find that *p*-di-iodobenzene yields *p*-di-iododiphenyl, benzene, and diphenyl, the formation of the last-named two substances being due to the decomposition of the dimagnesium compound, as shown by the following scheme:

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[40] H. Stobbe, A. Schwyzer, and G. S. Cruikshanks, *J. pr. Chem.*, 1914, [ii], **89**, 184, 189; *A.*, i, 540, 541.

[41] *Monatsh.*, 1914, **35**, 311; *A.*, i, 693.

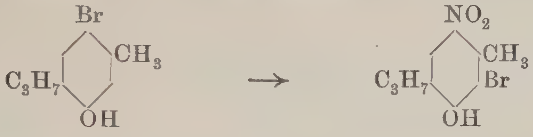
[42] *Ber.*, 1914, **47**, 1219; *A.*, i, 763.

$$C_6H_6 \xleftarrow{H_2O} C_6H_4(MgI)_2 + C_6H_4I{\cdot}MgI =$$
$$MgI_2 + MgI{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}MgI \xrightarrow{H_2O} C_6H_5{\cdot}C_6H_5.$$

Intramolecular Change.

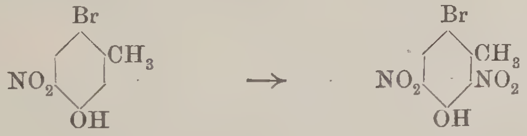
Whilst no new examples of the migration of atoms or groups have been recorded during the present year, several of those previously described have either been supported by further evidence or have been confirmed by the isolation of definite intermediate products.

The Migration of para-*Halogen Atoms in Phenols.*—The discovery by P. W. Robertson[43] that in the nitration of, for example, 6-bromothymol (I), the nitro-group displaces the halogen atom, which then migrates to the ortho-position, thus:

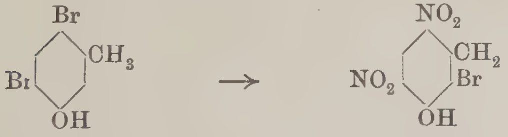


(I.)

has led to the investigation of other instances of the same kind. It is now found[44] that whereas 6-bromo-4-nitro-*m*-cresol (II) behaves normally on nitration, 4 : 6-dibromo-*m*-cresol (III) yields 2-bromo-4 : 6-dinitro-*m*-cresol (IV):



(II.)



(III.) (IV.)

The Migration of Acid Residues.—The phenomenon of migration of the acetyl group from oxygen to nitrogen during the reduction of certain acetylated azo-compounds has been established by K. v. Auwers and his collaborators. The migration seems to be affected, or entirely hindered, by the presence of certain groupings in the azo-molecule, and does not occur with the corresponding benzoyl derivatives. It has been shown[45] that the presence of a substituent in either nucleus prevents the transformation except in one instance, in which a methyl group occurred in the para-position of the benzene nucleus. Recent work[46] shows that the ethyl group in the same position also permits the migration.

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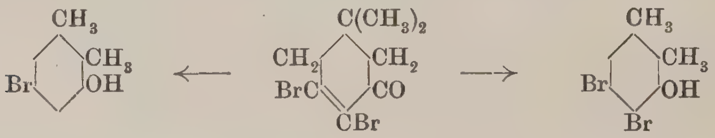
[43] *T.*, 1908, **93**, 793; P. W. Robertson and H. V. A. Briscoe, *ibid.*, 1912, **101**, 1961.

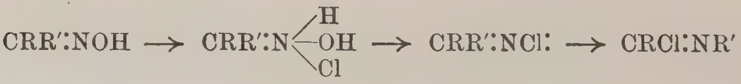
[44] I. R. Gibbs and P. W. Robertson, *ibid.*, 1914, **105**, 1885.

Aromatic from Hydroaromatic Substances.—The remarkable transformation of a hydroaromatic compound into a true aromatic derivative which is illustrated by the formation of brominated xylenols from dimethyldihydroresorcin by the action of phosphorus pentabromide,[47] has been further investigated by A. W. Crossley and Miss N. Renouf.[48] It is evidently the intermediate compound dibromodimethyl*cyclo*hexenone (I), that gives rise to the aromatic derivatives, since when this substance is treated with potassium hydroxide it is converted into 5-bromo-*o*-3-xylenol (II) mixed with small quantities of 4:5-dibromo-*o*-3-xylenol (III):



(II.) (I.) (III.)

The Beckmann Rearrangement.—J. Stieglitz and P. N. Leech[49] put forward an explanation of the Beckmann change, which differs from that of Hantzsch in assuming that at one stage a compound is produced containing a nitrogen atom having free residual valencies, thus:



$$CRR'{:}NOH \rightarrow CRR'{:}N\begin{smallmatrix}/H\\-OH\\\backslash Cl\end{smallmatrix} \rightarrow CRR'{:}NCl{:} \rightarrow CRCl{:}NR'$$

The last substance then undergoes hydrolysis in the usually accepted manner with the formation of an amide. This view is based on the similar behaviour of triarylmethylhydroxylamines, for example, triphenylmethylhydroxylamine, $CPh_3{\cdot}NH{\cdot}OH$, which on treatment with phosphorus pentachloride in ethereal solution is almost quantitatively converted into benzophenoneanil hydrochloride, $CPh_2{:}NPh,HCl$.

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[45] *Annalen*, 1909, **365**, 278; *A.*, 1909, i, 436.

[46] K. v. Auwers and F. Michaelis, *Ber.*, 1914, **47**, 1297; *A.*, i, 747.

[47] A. W. Crossley and H. R. Le Sueur, *T.*, 1903, **83**, 110.

[48] *T.*, 1914, **105**, 166.

[49] *J. Amer. Chem. Soc.*, 1914, **36**, 272; *A.*, i, 268.

Catalytic Reactions.

The hydrogenation of diarylacetones and aryl alcohols has been investigated by P. Sabatier and M. Murat.[50] Benzophenone and its homologues readily undergo hydrogenation in the presence of slightly active nickel at temperatures from 300° to 350°, giving the corresponding diaryl-hydrocarbons. At lower temperatures and with very active nickel, the aromatic nucleus also undergoes hydrogenation.

A. Mailhe[51] has prepared a number of new ketones by passing the mixed vapour of several pairs of acids over ferric oxide at 470—480°. In this way benzoic and phenylacetic acids yield phenyl benzyl ketone, $CH_2Ph\cdot COPh$, acetic and anisic acids yield anisyl methyl ketone, and so forth. The method, which can also be carried out in the presence of manganous oxide,[52] seems to be of general application. It is pointed out[53] that manganous oxide can also be used with advantage in place of titanic oxide for the preparation of aldehydes from the mixed vapours of formic with aliphatic or arylacetic acids. An application of this catalytic method of condensation is also seen in the formation of certain ether oxides of carvacrol.[54] It is found, for example, that when an equimolecular mixture of phenol and carvacrol vapours is passed over thorium oxide at 470—480°, phenyl carvacryl oxide is formed.

An interesting observation has been made by E. Knoevenagel,[55] who finds that in the preparation of thiodiarylamines by the action of sulphur on diarylamines, the addition of 0·05—2 per cent. of iodine not only causes the reaction to take place at a lower temperature, but also yields a purer product, and considerably shortens the time required for the completion of the reaction. A similar effect has been observed in the following reactions: (1) The formation of arylnaphthylamines by the condensation of aromatic amines with the naphthols and naphthylamines; (2) the alkylation of aniline and α-naphthylamine by the direct action of alcohols; (3) anil-formation with ketones and aromatic amines; (4) sulphonation; and (5) oxidation.

It has been found[56] that the bromination of benzene proceeds at a lower temperature in the presence of manganese, and that the ratio of recovered benzene to brominated benzene is 8 : 9 in the presence of manganese and 10 : 3 in its absence. Similar effects are observed in the bromination of toluene and the xylenes in the cold, but at higher temperatures better results are obtained without manganese.

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[50] *Compt. rend.*, 1914, **158**, 760; *A.*, i, 548.

[51] *Bull. Soc. chim*, 1914, [iv], **15**, 324; *A.*, i, 548.

[52] P. Sabatier and A. Mailhe, *Compt. rend.*, 1914, **158**, 830; *A.*, i, 547.

[53] *Ibid.*, 985; *A.*, i, 547.

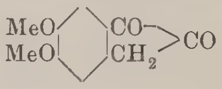
[54] *Ibid.*, 608; *A.*, i, 400.

[55] *J. pr. Chem.*, 1914, [ii], **89**, 1; *A.*, i, 519.

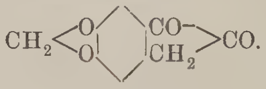
[56] L. Gay, F. Ducelliez, and A. Raynaud, *Compt. rend.*, 1914, **158**, 1804; *A.*, i, 946.

Ketones.

The important process for producing 1:2-diketohydrindene by the hydrolysis of oximino-1-hydrindone by means of formaldehyde and hydrochloric acid[57] has now[58] been applied, with even better results, to the preparation of 1:2-diketo-5:6-dimethoxyhydrindene (I) and 1:2-diketo-5:6-methylenedioxyhydrindene (II):



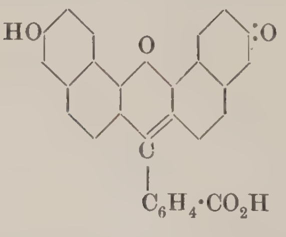
(I.)



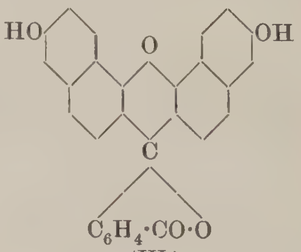
(II.)

These substances may very possibly find an application in solving the difficult problem of the synthesis of brazilin and its derivatives.

An important addition to the number of desmotropic substances related to the phthaleins has been made by O. Fischer and E. König,[59] who have succeeded in preparing a fluoran derivative, in both the lactone and quinonoid forms, by the action of phthalic anhydride on 1:6-dihydroxynaphthalene. Since this substance, from its mode of formation, must be derived from either an αβ- or a βα-naphthafluoran, and since it yields bisazo-dyes which do not dissolve in alkali, it follows that the lactone and quinonoid forms are represented by formulæ III and IV respectively:



(IV.)



(III.)

The lactone form is unstable, and can only be obtained colourless in solution or, in solid form containing two molecules of the solvent ($C_{28}H_{16}O_5,2Et_2O$; $C_{28}H_{16}O_5,2COMe_2$, and so forth). When deprived of the solvent of crystallisation, it passes over into the red quinonoid form.

A new method of methylation applicable to aliphatic and hydroaromatic ketones and esters of ketonic acids has been described.[60] The ketone is converted into the hydroxymethylene compound (V), which is then reduced by hydrogen in the presence of colloidal palladium to the methyl derivative (VI):

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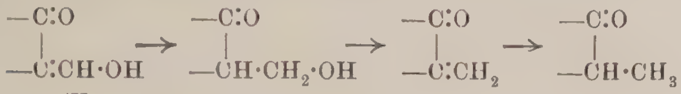
[57] W. H. Perkin, jun., W. M. Roberts, and R. Robinson, *T.*, 1912, **101**, 232.

[58] *Ibid.*, 1914, **105**, 2405.

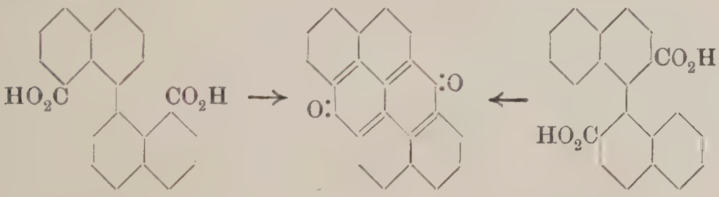
[59] *Ber.*, 1914, **47**, 1076; *A.*, i, 712.



$$\begin{array}{l} -\mathrm{C{:}O} \\ \;| \\ -\mathrm{C{:}CH{\cdot}OH} \end{array} \longrightarrow \begin{array}{l} -\mathrm{C{:}O} \\ \;| \\ -\mathrm{CH{\cdot}CH_2{\cdot}OH} \end{array} \longrightarrow \begin{array}{l} -\mathrm{C{:}O} \\ \;| \\ -\mathrm{C{:}CH_2} \end{array} \longrightarrow \begin{array}{l} -\mathrm{C{:}O} \\ \;| \\ -\mathrm{CH{\cdot}CH_3} \end{array}$$

(V.) (VI.)

Owing to their importance in connexion with the production of vat colouring matters, many new polycyclic quinones have been prepared and described. They do not call for any special mention excepting perhaps the compound (IX), to which the name anthanthrone has been given.[61] The structure of this substance is placed beyond dispute by the fact that it is prepared both from 1:1′-dinaphthyl-8:8′-dicarboxylic acid (VII) and from 1:1′-dinaphthyl-2:2′-dicarboxylic acid (VIII) by the dehydrating action of sulphuric acid:



(VII.) (IX.) (VIII.)

Benzhydrol.—A résumé of the chemistry of this substance is given by J. Sabatier and M. Murat,[62] who have attempted to prepare it by the action of water on the Grignard compound, $\mathrm{CHPh_2{\cdot}OMgBr}$. They obtained, however, a yield of only 3 per cent., the main products being diphenylmethane and *s*-tetraphenylethane; since benzophenone is also formed, it is assumed that the reaction is represented by the equations:

$$3\mathrm{CHPh_2{\cdot}OH} = 2\mathrm{H_2O} + \mathrm{COPh_2} + \mathrm{CHPh_2{\cdot}CHPh_2}.$$
$$2\mathrm{CHPh_2{\cdot}OH} = \mathrm{H_2O} + \mathrm{COPh_2} + \mathrm{CH_2Ph_2}.$$

In a later paper the same authors[63] show that a nearly theoretical yield of benzhydrol can be obtained by the action of benzaldehyde on magnesium phenyl bromide.

It is of interest to note that benzhydrol derivatives containing a substituted amino-group in the para-position are split by bromine, forming aldehydes and bromo-substituted anilines.[64] The reaction is probably represented in the following manner:

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[60] A. Kötz and E. Schaeffer, *J. pr. Chem.*, 1913, [ii], **88**, 604; *A.*, i, 186; J. D. Riedel, D.R.-P. 266405; *A.*, i, 186.

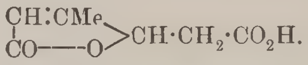
[61] L. Kalb, *Ber.*, 1914, **47**, 1724; *A.*, i, 849.

[62] *Compt. rend.*, 1913, **157**, 1496; *A.*, i, 168.

[63] *Ibid.*, 1914, **158**, 534; *A.*, i, 404.

$$\mathrm{OH{\cdot}CHPh{\cdot}C_6H_4{\cdot}NR_2 \longrightarrow OH{\cdot}CHPh{\cdot}C_6H_4{\cdot}NR_2Br_2 \longrightarrow}$$
$$\mathrm{OH{\cdot}CHPh{\cdot}NR_2Br{\cdot}C_6H_4Br \longrightarrow CHPhO + C_6H_4Br{\cdot}NR_2,HBr.}$$

Rupture of the Benzene Ring without Degradation.—The rupture of the benzene nucleus which is illustrated by the formation of acetylacrylic acid by the action of fuming sulphuric acid on 3-nitro-*p*-cresol[65] has been re-investigated by H. Pauly, R. Gilmour, and G. Will.[66] They find that the acid $C_7H_8O_4$, which is produced in this reaction, is not acetylacrylic acid, but β-methyl-γ-crotonolactone-γ-acetic acid:



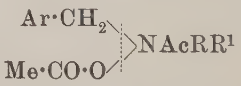
$$\begin{array}{l}\mathrm{CH{:}CMe}\\ |\\ \mathrm{CO{-}{-}{-}O}\end{array}\!\!>\mathrm{CH{\cdot}CH_2{\cdot}CO_2H.}$$

The course of the reaction is merely hydrolytic; 3-nitro-*p*-cresol reacts, in the first instance, in its isomeric form, that is, as the nitrolic acid, and is hydrolysed to the hydroxamic acid,

$$\mathrm{CO_2H{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}C(OH){:}NOH.}$$

This is then further hydrolysed to hydroxylamine and β-methylmuconic acid, which subsequently passes into the lactone and water. The nitrogenous by-product, which is also formed,[67] and has the structure $C_7H_7O_3N$, is regarded as 2-hydroxy-4-methylpyridine-6-carboxylic acid, and is formed from the hypothetical hydroxamic acid mentioned above by loss of water and ring closure.

The Fission of Tertiary Bases.—The fission of tertiary bases at the nitrogen atom by cyanogen bromide which was studied by J. v. Braun,[68] showed that the reaction was most marked when the amine contained a benzyl group. M. Tiffeneau and K. Fuhrer [69] have now investigated the fission of bases by means of acid anhydrides and acid chlorides, and find that the fission can only be effected in those cases in which the base has the structure $\mathrm{Ar{\cdot}CH_2{\cdot}NRR'}$. The action is attributed to the intermediate formation of compounds of the type:



$$\begin{array}{r}\mathrm{Ar{\cdot}CH_2}\diagdown\\ \mathrm{Me{\cdot}CO{\cdot}O}\diagup\end{array}\!\vdots\!>\mathrm{NAcRR^1}$$

which undergo fission on heating in the manner shown by the dotted line.

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[64] G. J. Esselen, jun. and L. Clarke, *J. Amer. Chem. Soc.*, 1914, **36**, 308; *A.*, i, 278.

[65] G. Schultz and O. Löw, *Ber.*, 1909, **42**, 577; *A.*, 1909, i, 222.

[66] *Annalen*, 1914, **403**, 119; *A.*, i, 485.

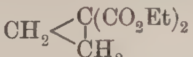
[67] G. Schultz and O. Löw, *Ber.*, 1910, **43**, 1899; *A.*, 1910, i, 552.

[68] *Ber.*, 1900, **33**, 1438, 2728, 2734, 2965; *A.*, 1900, i, 430, 641, 687.

[69] *Bull. Soc. chim.*, 1914, [iv], **15**, 162; *A.*, i, 517.

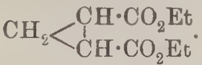
Carbon-ring Formation.

A systematic study of this important question has been started,[70] and it is evident that we have still much to learn respecting the conditions which control the formation of cyclic compounds from open carbon chains. It is certain that whereas the Baeyer "Spannungstheorie" serves, and has served, as a good working hypothesis, it is merely that and nothing more, since the tendency to ring-formation exhibited by carbon chains depends not only on the angle of the particular ring, but also to a very considerable extent on the condition of the carbon atoms forming the chain. An admirable summary of some of the more salient facts, and a likely explanation is given by J. Kenner,[71] but it is evident that much work remains to be done before this question can be completely answered. There can be no doubt that the presence in the open-chain compound of a carbon atom which, in the resulting ring compound, will be quaternary, has a marked influence against the tendency to ring-formation. There are numerous examples illustrating the truth of this statement, and perhaps the simplest and best is that given by L. J. Goldsworthy and W. H. Perkin,[72] who point out that the yield of ethyl *cyclo*propane 1 : 1-dicarboxylate (I) from ethylene dibromide and the sodium derivative of ethyl malonate is very small, whereas ethyl *cyclo*propane-1 : 2-dicarboxylate (II) is readily prepared in good yield by a similar method:



$$CH_2{<}\begin{array}{l}C(CO_2Et)_2\\ CH_2\end{array}$$

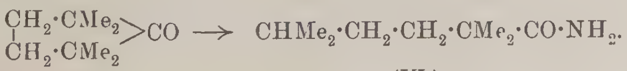
(I.)



$$CH_2{<}\begin{array}{l}CH{\cdot}CO_2Et\\ CH{\cdot}CO_2Et\end{array}.$$

(II.)

It follows, therefore, that rings containing a quaternary carbon atom are relatively less stable than those in which a carbon atom of this kind is absent. This point is well brought out by Kenner,[73] and is also illustrated by the two compounds mentioned above, because, whereas ethyl *cyclo*propane-1 : 1-dicarboxylate (I) is readily split by hydrogen bromide, the ester (II) is very stable towards this reagent. It is interesting to note that still another example of this kind has been recorded during the year, namely, that given by A. Haller and R. Cornubert[74] in the production of $\alpha\alpha\delta$-trimethylhexamide (IV) from 1 : 1 : 3 : 3-tetramethyl*cyclo*pentan-2-one (III) by the action of sodamide:



$$\begin{array}{l}CH_2{\cdot}CMe_2\\ CH_2{\cdot}CMe_2\end{array}{>}CO \longrightarrow CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CO{\cdot}NH_2.$$

(III.) (IV.)

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[70] L. J. Goldsworthy and W. H. Perkin, jun., *T.*, 1914, **105**, 2665.

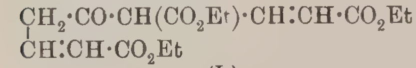
[71] *T.*, 1914, **105**, 2685.

[72] *Loc. cit.*

[73] *Loc. cit.*, p. 2689.

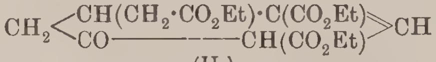
[74] *Compt. rend.*, 1914, **158**, 298 ; *A.*, i, 291.

Cyclic Compounds from Ethyl Glutaconate.—The condensation of two molecules of ethyl glutaconate under the influence of condensing agents has been studied by E. E. Blaise[75] and by H. v. Pechmann.[76] The first-named, using sodium ethoxide at 100°, obtained a compound which he considered to have formula (I), whereas v. Pechmann and his collaborators, working in ethereal solution, obtained a compound to which either formula (II) or (III) was assigned:



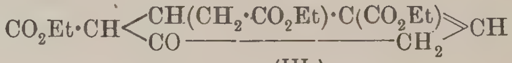
$$\begin{array}{l}CH_2\cdot CO\cdot CH(CO_2Et)\cdot CH{:}CH\cdot CO_2Et\\ |\\ CH{:}CH\cdot CO_2Et\end{array}$$

(I.)



$$CH_2{<}\begin{array}{l}CH(CH_2\cdot CO_2Et)\cdot C(CO_2Et)\\ CO\text{————}CH(CO_2Et)\end{array}{>}CH$$

(II.)

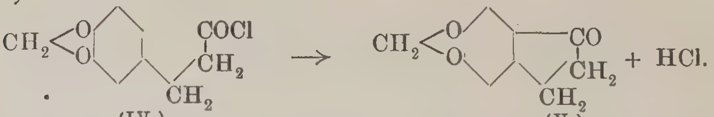


$$CO_2Et\cdot CH{<}\begin{array}{l}CH(CH_2\cdot CO_2Et)\cdot C(CO_2Et)\\ CO\text{——————}CH_2\end{array}{>}CH$$

(III.)

The two compounds melted at much the same temperature, but apparently differed in some of their properties. It is now found[77] that the compounds prepared by the two methods are identical, and that, of formulæ II and III, the latter is the more probable.

The formation of ring structures by the spontaneous decomposition of acid chlorides, which was originally investigated by W. Borsche and his co-workers,[78] has been extended[79] to the preparation of hydrindone derivatives. An example of this method, which is of importance since it renders the use of aluminium chloride unnecessary, may be given in the formation of methylenedioxy-α-hydrindone (V) by the distillation of piperonylpropionyl chloride (IV):



(IV.) (V.)

It is stated that, contrary to the views expressed by others,[80] the elimination of hydrogen chloride in this manner is not greatly influenced by the presence of phosphorus compounds.

It is well known that the five-carbon ring is usually formed with the greatest ease and in the presence of the mildest reagents, but that slight changes in the structure of the open-chain compound sometimes either hinder or entirely prevent the closing of the ring. An instance of this kind is recorded by E. E. Blaise,[81] who finds that *s*-dipropionylethane (VI) is readily converted into 1-methyl-2-ethyl-Δ^1-*cyclo*penten-6-one (VII) by 10 per cent. aqueous potassium hydroxide:

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[75] E. E. Blaise, *Compt. rend.*, 1903, **136**, 639; *A.*, 1903, i, 400, 548.

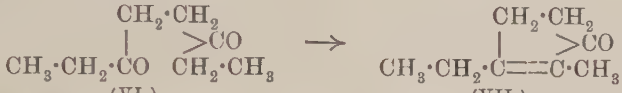
[76] H. v. Pechmann, W. Bauer, and J. Obermiller, *Ber.*, 1904, **37**, 2113; *A.*, 1904, i, 592.

[77] R. Curtis and J. Kenner, *T.*, 1914, **105**, 282.

[78] *Ber.*, 1911, **44**, 2942; *A.*, 1911, i, 1018.

[79] W. Borsche and W. Eberlein, *ibid.*, 1914, **47**, 1460; *A.*, i, 699.

[80] H. Leuchs, J. Wutke, and E. Gieseler, *ibid.*, 1913, **46**, 2200; *A.*, 1913, i, 855; H. Lecher, *ibid.*, 2664; *A.*, 1913, i, 1166.



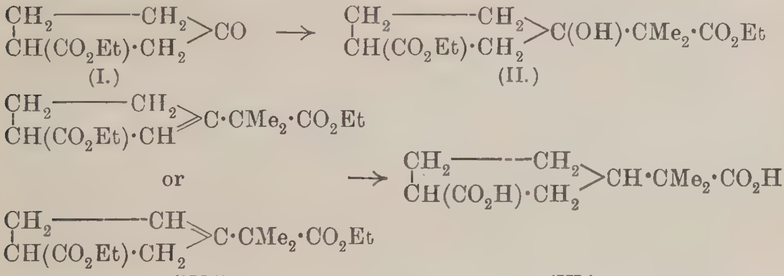
$$\begin{array}{l} \qquad\qquad CH_2{\cdot}CH_2 \\ \qquad\qquad \;| \qquad\; >CO \\ CH_3{\cdot}CH_2{\cdot}CO \quad CH_2{\cdot}CH_3 \end{array} \longrightarrow \begin{array}{l} \qquad\qquad CH_2{\cdot}CH_2 \\ \qquad\qquad \;| \qquad\; >CO \\ CH_3{\cdot}CH_2{\cdot}C{=\!=\!=}C{\cdot}CH_3 \end{array}$$

(VI.) (VII.)

whereas acetonylacetone and acetonylacetophenone are quite unchanged under these conditions.

Terpenes and Allied Compounds.

Camphenic Acid.—The structure assigned to this acid by Aschan[82] has been verified by its synthesis.[83] Ethyl *cyclo*pentan-1-one-3-carboxylate (I) is condensed with ethyl α-bromo*iso*butyrate in the presence of zinc, when ethyl 3-carbethoxy*cyclo*pentan-1-ol-1-*iso*butyrate (II) is produced. The elimination of water from this substance by the aid of potassium hydrogen sulphate gives the ethyl ester (III) of either 3-carboxy-Δ^1- or Δ^5-*cyclo*pentene-1-*iso*butyric acid, and when the free acid from this is reduced by hydrogen and platinum black, *dl-cis*-camphenic acid, that is, 3-carboxy*cyclo*pentane-1-*iso*butyric acid (IV), is produced:



$$\begin{array}{l} CH_2\text{———}CH_2 \\ |\qquad\qquad\qquad\;\; >CO \\ CH(CO_2Et){\cdot}CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2\text{———}CH_2 \\ |\qquad\qquad\qquad\;\; >C(OH){\cdot}CMe_2{\cdot}CO_2Et \\ CH(CO_2Et){\cdot}CH_2 \end{array}$$

(I.) (II.)

$$\begin{array}{l} CH_2\text{———}CH_2 \\ |\qquad\qquad\qquad\;\; >C{\cdot}CMe_2{\cdot}CO_2Et \\ CH(CO_2Et){\cdot}CH \\ \qquad\qquad \text{or} \\ CH_2\text{———}CH \\ |\qquad\qquad\qquad\;\; >C{\cdot}CMe_2{\cdot}CO_2Et \\ CH(CO_2Et){\cdot}CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2\text{———}CH_2 \\ |\qquad\qquad\qquad\;\; >CH{\cdot}CMe_2{\cdot}CO_2H \\ CH(CO_2H){\cdot}CH_2 \end{array}$$

(III.) (IV.)

The synthesis of camphenic acid in this manner removes the last doubt as to the correctness of the Wagner formula for camphene. Wagner himself[84] suggested that the remarkable change from the borneol to the camphene structure could be regarded as similar to that which occurs in the pinacolin rearrangement. Meerwein[85] has now brought forward evidence which shows that this explanation is correct. He points out that the transformation of borneol into camphene can be represented thus:

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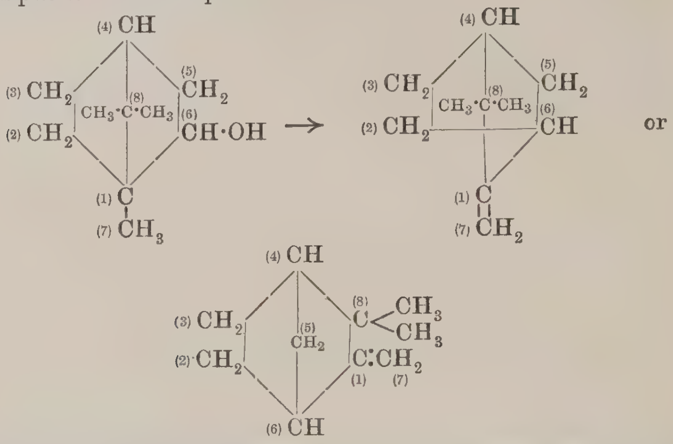
[81] *Compt. rend.*, 1914, **158**, 708; *A.*, i, 546.

[82] *Annalen*, 1910, **375**, 336; 1911, **383**, 52; *A.*, 1910, i, 709; 1911, i, 797.

[83] P. Lipp, *Ber.*, 1914, **47**, 871; *A.*, i, 542.

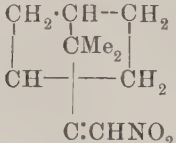
[84] *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 680.

[85] *Annalen*, 1914, **405**, 129; *A.*, i, 850.

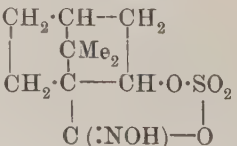


that is to say, the five-carbon ring 1, 2, 3, 4, 8 passes, owing to the shifting of the carbon atom 6, into a hexamethylene ring, whilst at the same time the *cyclo*hexane structure composed of the carbon atoms 1 to 6 passes, owing to the elimination of the carbon atom 1, into a pentamethylene ring. The view is supported by numerous experiments, in which water is eliminated from compounds similar to borneol in structure.

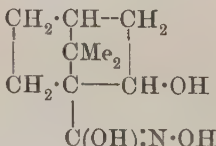
Another example of the conversion of camphene into camphane derivatives is recorded by P. Lipp.[86] During the course of some experiments on the conversion of nitrocamphene (V) into tricyclenic acid,[87] it was found that the nitrogen is eliminated in the form of hydroxylamine, suggesting, therefore, the intermediate formation of a hydroxamic acid. Actually the first product of the reaction is a neutral sulphuric ester, $C_{10}H_{15}O_5NS$, which, when hydrolysed, yields camphenylhydroxamic acid (VII). The sulphuric ester has therefore the formula VI:



(V.)



(VI.)



(VII.)

The Wallach formula for fenchocamphorone has been established by its synthesis[88] from homo*apo*camphoric acid. When the lead salt of this acid is distilled in a current of carbon dioxide *r*-fenchocamphorone is produced:

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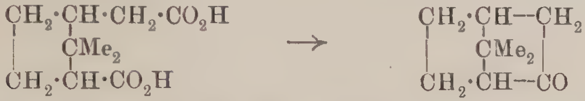
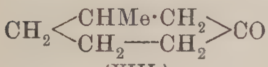
[86] *Annalen*, 1914, **402**, 343; *A.*, i, 305.

[87] J. Bredt and R. May, *Chem. Zeit.*, 1909, **33**, 1265; *A.*, 1910, i, 32.

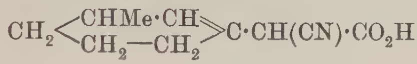
[88] G. Komppa, *Ber.*, 1914, **47**, 933; *A.*, i, 556.



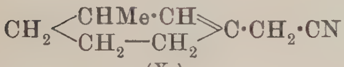
Hydrocarbons Allied to the Terpenes.—A method has been described[89] by which the action of the Grignard reagent on nitriles may be utilised for the production of certain hydrocarbons allied to the terpenes. Thus the condensation of 1-methyl*cyclo*hexan-3-one (VIII) with the sodium compound of ethyl cyanoacetate leads, in part, to the formation of the cyano-acid (IX). Elimination of carbon dioxide yields the nitrile (X), from which by the action of magnesium methyl iodide the ketone (XI) is produced. Further treatment with the Grignard reagent then yields the terpineol (XII), which gives the hydrocarbon (XIII) on dehydration:



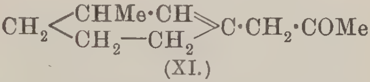
(VIII.)



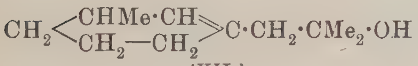
(IX.)



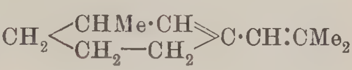
(X.)



(XI.)

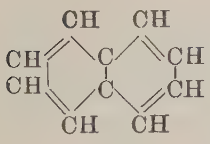


(XII.)

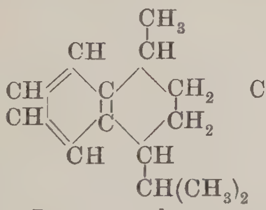


(XIII.)

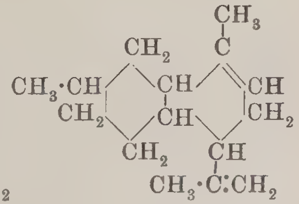
Benzoterpenes.—A series of experiments has been started[90] with the object of synthesising substances having a similar structure to the terpenes, but containing an aromatic residue (XIV). It is thought that a study of these substances will help to elucidate the problem of the structure of the sesquiterpenes, since the relationship between naphthalene and the hydroaromatic sesquiterpenes is shown by the following formulæ:



Naphthalene.



Benzo-*p*-menthane.
(XIV.)



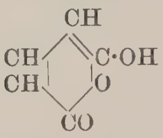
a-Selinene.

[89] W. N. Haworth and A. W. Fyfe, *T.*, 1914, **105**, 1659.
[90] F. W. Kay and A. Morton, *ibid.*, 1565.

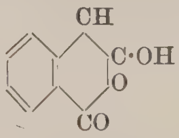
It is open to question whether any useful purpose is served by giving the name benzo-*p*-menthane to a substance which is obviously a true derivative of tetrahydronaphthalene.

Various Reactions.

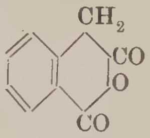
The tendency to the formation of hydroxy-anhydrides (6-hydroxy-α-pyrones) from glutaconic acid and some of its derivatives, which was described by N. Bland and J. F. Thorpe,[91] has been shown by W. Dieckmann[92] to be exhibited also by homophthalic acid (II). A comparison of the hydroxy-anhydrides of homophthalic acid and glutaconic acid (I) shows that both yield yellow neutral salts with alkali, but that the anhydride from homophthalic acid gives no colour with ferric chloride and does not absorb bromine. In the free state it has, therefore, the normal structure (III):



(I.)

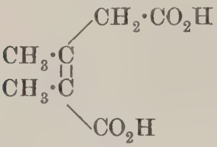


(II.)

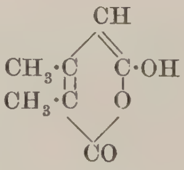


(III.)

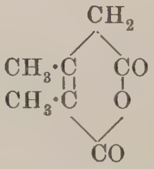
Homophthalic acid is therefore comparable with, for example, αβ-dimethylglutaconic acid[93] (IV), which, although it yields an anhydride that dissolves in alkali, does not give a coloration with ferric chloride, and thus according to Dieckmann should, in the free state, have the structure VI:



(IV.)



(V.)



(VI.)

There is, of course, a fallacy in Dieckmann's argument, for if the anhydride of glutaconic acid has the enol structure *because* it gives a yellow sodium salt and a coloration with ferric chloride, why is the free anhydride colourless? This error is apparent in a great deal of the work that has been done recently on keto-enol tautomerism. It has been too hastily assumed that, because the ferric chloride and bromine-absorption reactions serve as excellent means for distinguishing between the keto and enol forms of certain types, therefore, when compounds fail to respond to these tests, the absence of the enol modification is proved. It must be remembered that, of the two isomeric phenols thymol and carvacrol, only carvacrol gives a coloration with ferric chloride, and there are,

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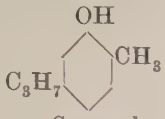
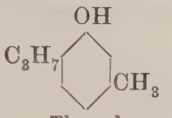
[91] *T.*, 1912, **101**, 863.

[92] *Ber.*, 1914, **47**, 1428; *A.*, i, 690.

[93] F. B. Thole and J. F. Thorpe, *T.*, 1911, **99**, 2216.



Carvacrol.



Thymol.

moreover, numerous other examples which show that whereas a positive ferric chloride reaction is a sure indication of the presence of the enol variety, a negative result does not necessarily show its absence.

Reduction of the Carbonyl Group.—The valuable method for the reduction of aldehydes and ketones which was introduced by E. Clemmensen[94] has now been improved and extended.[95] The method promises to be of special service in the preparation of homologues of the various phenols from hydroxy-ketones, and although its value for the reduction of hydroxy-aldehydes is diminished by the sensitiveness of many of these compounds towards hydrochloric acid, the methyl-substituted phenols obtained are of a high degree of purity. The ketones are reduced by amalgamated zinc in the presence of hydrochloric acid, and the applicability of the method is illustrated by the production of numerous substituted phenols from the corresponding ketones; thus *p*-hydroxyacetophenone yields *p*-ethylphenol, *m*-acetyl-*o*-cresol gives 2-methyl-4-ethylphenol, acetylquinol is reduced to ethylquinol, and so forth.

Esterification by Ultra-violet Light.—It has been noticed during the course of certain experiments having for their object the transformation of stereoisomerides by ultra-violet light,[96] that alcoholic solutions of certain acids undergo esterification when exposed to these rays. Thus benzoic acid is esterified to the extent of 30 per cent. in eight days, and to the extent of 56 per cent. in the same time when a trace of hydrochloric acid is present.

Phototropy and Thermotropy.—That trituration or rubbing is capable of producing polymorphic change and is an important means of bringing about chemical reactions is well known, and the paper recently communicated by L. H. Parker[97] not only adds to our knowledge of this subject, but also contains a useful list of references to previous work. The principle has now been applied[98] to a number of 4-hydroxybenzylidenearylamines, the general results of which may be described by referring to those obtained with 4-hydroxybenzylideneaniline, $OH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_5$. This substance is dimorphous; trituration changes it into a deeper-coloured dimorphic variety, which, however, on long keeping reverts to the original compound. The paler-coloured variety is thermotropic, becoming paler at "the lower temperature" (that is, of solid carbon dioxide), and returning to the original colour at the ordinary temperature. The deeper-coloured variety is not phototropic, but on prolonged exposure to sunlight changes to a brown, polymorphic form.

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[94] *Ber.*, 1913, **46**, 1837; *A.*, 1913, i, 733.

[95] E. Clemmensen, *ibid.*, 1914, **47**, 51; *A.*, i, 271.

[96] R. Stoermer and H. Ladewig, *ibid.*, 1803; *A.*, i, 966.

[97] *T.*, 1914, **105**, 1504.

[98] A. Senier and R. B. Forster, *ibid.*, 2462.

J. F. THORPE.

PART III.—HETEROCYCLIC DIVISION.

IN former years, the task of the reporter was rendered difficult by the great mass of material from which it was necessary to select those subjects which lent themselves best to summarisation in brief; but in the current Report this embarrassment has not been so great as usual, for only the first seven months of the year's work are covered by the Austrian and German journals in our possession, so that the amount of published matter to be dealt with is less than in any previous year. This has necessitated a choice between two policies, for it was possible either to make the Report of the customary length by including various pieces of work of less importance, or to reduce the length of the Report to some extent and keep its standard approximately the same as in other volumes. The latter objective has been chosen, as it seems the more desirable of the two, so that the present Report remains comparable with its forerunners.

Last year saw the close of the main investigations on the constitution of chlorophyll, and in the period covered by this Report it cannot be said that much more light has been thrown on the broad outlines of the problem. The work of the year in this particular field has taken a fresh turn, and the researches of various investigators have been directed towards the occurrence of chlorophyll in various plants, and the reactions of chlorophyll *qua* chlorophyll, rather than those of its decomposition products. In fact, it may be said that chlorophyll at present is falling back from the centre of the chemical stage and giving place to other subjects of interest.

The same holds good with regard to the chemistry of the blood pigment. Great advances in our knowledge of this substance were made in 1913, but the last twelve months have left the main question very much where it was, and have been spent in that slow and laborious work which marks the accumulation of data that are necessary before a further advance is possible. This amassing of isolated facts does not lend itself to reproduction in connected form, so that in the present Report only a brief mention is made of some points; but it must be borne in mind that those fields which have been selected for treatment represent only a small fraction of the work accomplished in the twelvemonth, and it must not be assumed that the investigation of hæmin is approaching a standstill.

Hæmin and chlorophyll having thus passed into a new stage of their chemical career, we turn to another field to find the subject which promises to take their place. From the developments which have recently occurred, it appears likely that this will be found in the study of the pigments of plants and flowers. In fact, as far as the heterocyclic series is concerned, this year has been marked by a greater advance in this direction than any which have taken place in other branches of the subject. Willstätter and his colleagues have not only broken new ground, but have already established the main lines along which further advances can be made, and, what is even more encouraging than the success of a single school, many other workers have been drawn into the field in question, so that it appears certain that our knowledge of it will soon progress both extensively and intensively.

These developments in the study of chlorophyll, hæmin, and the plant pigments appear to mark the recrudescence of organic chemistry proper, in contradistinction from what may be termed the chemistry of the carbon compounds. Thus pure chemistry and physiological chemistry are again tending to become more closely allied than they have been since the earliest days of modern chemical history, and this approximation appears one of the most hopeful signs in present-day science. Under the conditions existing in living organisms, many reactions take place at the ordinary temperature which in the laboratory can only be brought about by the use of active reagents and the application of heat, and it seems possible that the coming years may see determined attempts to reproduce these reactions under conditions more similar to those which suffice for the syntheses of compounds within vital tissues.

Turning now to fields of less general interest, the investigations of hæmin and chlorophyll have necessitated a closer investigation of the pyrrole group, and a considerable amount of work has been carried out in this branch of the subject during the year, although much of it is too detailed to summarise in these pages.

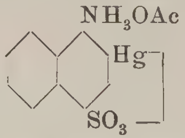
The chemistry of the alkaloids has not been marked by any great advances, but rather by a steady accumulation of knowledge upon minor points, which will serve its purpose later on.

New syntheses of coumarin and thiophen have been devised, of which the latter is important, as it permits of the substance being obtained in quantity with ease, and it seems likely our knowledge of the thiophen group may soon increase considerably. Another point to which attention might be drawn is the discovery that pyridine acts on many sulphur compounds catalytically, so that it is a solvent that must be utilised with caution for substances of this type.

Surveying the heterocyclic group as a whole, it cannot be said that the year has been by any means an unsatisfactory one as regards research in this division of the subject.

Cyclic Compounds the Rings of which contain Mercury Atoms.

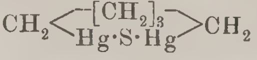
The number of elements which have hitherto shown a tendency to act as members of heterocyclic rings is comparatively limited, and it is therefore of some interest to find that this year has brought an increase in this class. Not only do we find mercury atoms playing the part of ring-members in the case of substances such as



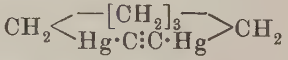
in which the heterocyclic ring is produced by a kind of internal salt-formation, akin to the betaine or lactone structure, but compounds have been synthesised which are mercury analogues of piperidine or penthiophen, and in some cases more than one mercury atom occupies a place in the ring.[1]

The preparation of the dimercuri-compounds begins with the production of a Grignard reagent from αε-dibromopentane. The magnesium compound is then treated in ethereal solution with dry, powdered mercuric bromide, and by this means pentamethylene-αε-dimercuridibromide is quantitatively formed. In this compound, the mercury atoms are very firmly attached to the rest of the molecule, whilst the halogen atoms are extremely reactive, so that the corresponding iodide, nitrate, or hydroxide can be obtained from the dibromide.

The dibromide is also attacked by either hydrogen sulphide or acetylene, yielding compounds the simplest formulæ of which would be


$$\mathrm{CH_2}<\begin{matrix}-[\mathrm{CH_2}]_3-\\ \mathrm{Hg\cdot S\cdot Hg}\end{matrix}>\mathrm{CH_2}$$

and


$$\mathrm{CH_2}<\begin{matrix}-[\mathrm{CH_2}]_3-\\ \mathrm{Hg\cdot C{:}C\cdot Hg}\end{matrix}>\mathrm{CH_2}$$

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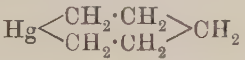
[1] R. Brieger and W. Schulemann, *J. pr. Chem.*, 1914, [ii], **89**, 97 ; *A.*, i, 611,

but as the molecular weight of these has not been ascertained, it is possible that they are polymerides.[2]

The bromine atoms are also replaceable by dibasic acid radicles, and in this way rings containing a very large number of atoms can be produced; for example, azelaic acid yields an eighteen-membered ring.

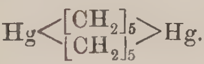
The action of magnesium phenyl bromide on the mercuribromide results in the production of pentamethylene-αε-dimercuridiphenyl, $Ph\cdot Hg\cdot[CH_2]_5\cdot HgPh$, a representative of a mixed mercury dialkyl.

Turning now to the problem of preparing cyclic compounds containing only a single mercury atom in the ring, it cannot yet be said that this problem has been placed beyond doubt, for the molecular-weight determinations seem to have been unsatisfactory, so that we cannot be certain that the substance produced has the formula I and not II:



$$\mathrm{Hg}\left<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\right>CH_2$$

(I.)



$$\mathrm{Hg}\left<\begin{matrix}[CH_2]_5\\ [CH_2]_5\end{matrix}\right>\mathrm{Hg}.$$

(II.)

The compound was prepared by the action of sodium amalgam on αε-dibromopentane. It appears to polymerise readily, thus showing an analogy to some cyclic compounds containing oxygen and sulphur atoms in the ring. Its most characteristic reaction is shown when it is treated with iodine, dihalogenopentanes and pentamethylene-αε-dimercury haloids being formed.

Thiophen and some of its Derivatives.

Hitherto the synthesis of thiophen has been a somewhat laborious one, but a new process has recently been discovered[3] whereby it may be produced in large quantities with the minimum of trouble. Pyrites is heated at about 300° in a tube through which acetylene is passed, and it is found that about half the product is thiophen, which can easily be purified from the by-products of the reaction. The essential condition for success is the employment of the pyrites in a very finely powdered state. When the apparatus is working properly, it is possible to prepare more than 300 grams of thiophen per diem.

The substitution of isoprene or βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene for acetylene gives rise to 3-methylthiophen and 3 : 4-dimethylthiophen respectively, but the yields are very poor.[4]

The nitration of thiophen has been studied, and it is found that when thiophen dissolved in acetic anhydride is nitrated at 0—5° by means of nitric acid (D 1·52) dissolved in acetic anhydride (air being drawn through the mixture during the operation), the product is 2-nitrothiophen in a 70 per cent. yield.

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[2] S. Hilpert and G. Grüttner, *Ber.*, 1914, **49**, 177, 186; *A.*, i, 261, 262.

[3] W. Steinkopf and G. Kirchhoff, *Annalen*, 1914, **403**, 1; *A.*, i, 425.

[4] W. Steinkopf, *ibid.*, 17; *A.*, i, 426.

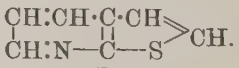
From the nitrothiophen thus formed, the corresponding aminothiophen can be obtained by reduction with tin and hydrochloric acid. It is not very stable, for in the presence of a trace of oxygen it polymerises, and subsequently undergoes oxidation.

The action of mercuric chloride on thiophen gives rise to both mono- and di-mercurichlorides. Investigations have now been set on foot to discover the influence on the reaction which is exerted by substituents in the thiophen nucleus.[5] When both α-positions of the thiophen ring are free, it is possible to obtain a dimercuri-derivative as well as the mono-compound, but if one α-position be occupied by a substituent, then, as a general rule, only the mono-mercurichloride is produced. When both the α-positions in the thiophen ring are substituted, the results of the reaction are different, for in some cases the end-product is an additive compound containing a mercurichloride group in position 3, whilst in other instances no interaction at all takes place between the substituted thiophen and the mercuric chloride. These rules are evidently subject to exceptions, and do not furnish us with a trustworthy method of differentiating between isomeric thiophen derivatives.

Thiophen-2-mercurichloride reacts with sodium in boiling xylene to form mercury 2 : 2′-dithienyl, $Hg(C_4H_3S)_2$.

This work has led to an interesting discovery of a method by means of which thiophen ketones can be prepared. Thiophen is allowed to react with mercuric chloride, producing thiophen-2-mercurichloride. By the action of acetyl chloride on the latter substance, 2-acetylthiophen is formed and mercuric chloride is eliminated. In this way, a small quantity of mercuric chloride should suffice to convert a large quantity of thiophen into the ketone, and a reaction somewhat akin to the Friedel-Crafts' synthesis has been discovered. The yields obtained are good, and the reaction appears to be generally applicable.

A compound of some interest has been synthesised which contains a thiophen nucleus condensed with a pyridine ring.[6] The method of preparation is a modification of Skraup's quinoline synthesis, 2-aminothiophen being substituted for aniline and 2-nitrothiophen being used instead of nitrobenzene. The yield is a poor one, 5—7 per cent. of pyridino-2 : 3-thiophen (I) being produced:



$$\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{\cdot}CH} \\ \mathrm{CH{:}N{-}C{-}S}\end{array}\!\!>\!\mathrm{CH}.$$

(I.)

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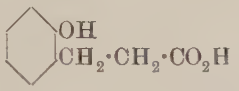
[5] W. Steinkopf and M. Bauermeister, *Annalen*, 1914, **403**, 50 ; *A.*, i, 427.

[6] W. Steinkopf and G. Lützendorf, *ibid.*, 45 ; *A.*, i, 432.

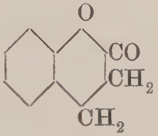
The substance is a yellow liquid resembling quinoline in its odour and in some of its reactions.

A Synthesis of Coumarin.

When a mixture of *o*-chlorobenzylidene chloride, acetic acid, and potassium acetate is heated at 210—220°, the product of the reaction is *o*-chlorocinnamic acid. This compound, by electrolytic reduction, can be converted into *o*-chloro-β-phenylpropionic acid, which, in turn, by heating with sodium hydroxide and water at 250°, is changed into melilotic acid (I):



(I.)



(II.)

Distillation of this substance produces the corresponding internal anhydride (II), and by passing bromine vapour over the last-named substance at a temperature of 270—300°, two atoms of hydrogen are removed in the form of hydrogen bromide, and coumarin is produced.[7]

The Condensation Products of Phloroglucinol and Aldehydes.

When three molecular proportions of phloroglucinol are condensed with two of an aldehyde, two molecular proportions of water are eliminated, but a careful examination of the products shows that in actual practice two reactions are taking place side by side, with the production of two different end-products.[8] The state of affairs may be expressed in the following manner:

Reaction I.	1 mol.	Phloroglucinol	+ 1 mol.	Aldehyde	− 1 mol.	Water.
,, II.	2 mols.	,,	+ 1 mol.	,,	− 1 mol.	,,
Total effect.	3 mols.	,,	+ 2 mols.	,,	− 2 mols.	,,

The course of the condensation is much affected by the conditions employed and by the nature of the condensing agent used. The initial condensation products are colourless and amorphous, but if they are kept in contact with the mother liquor a further elimination of water takes place, and red compounds are obtained. Thus when β-hydroxybutyraldehyde is condensed with phloroglucinol by means of dilute sulphuric acid at about 6°, the product has the composition $C_{10}H_{12}O_4$, and appears to have the structure

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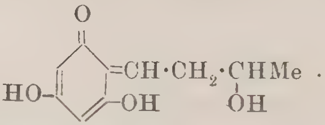
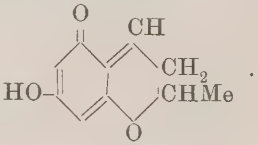
[7] H. Meyer, R. Beer, and G. Lasch, *Monatsh.*, 1913, **34**, 1665 ; *A.*, i, 44.

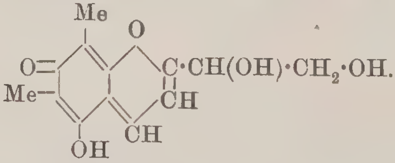
[8] F. Wenzel, *ibid.*, 1915 ; *A.*, i, 75.



This substance is deposited from the solution in snow-white flocks, which turn to a pale yellow powder on drying; but, if it is allowed to remain in contact with sulphuric acid for a time, it loses a second molecule of water and yields a red substance, which apparently has the structure represented by



The reaction appears to be a fairly general one, being applicable even in the case of the monosaccharoses and phloroglucinol. Thus *l*-xylose can be condensed with dimethylphloroglucinol in presence of hydrochloric acid to form a deep brownish-red substance, which appears to have the structure represented by



Some of these compounds appear to yield well-defined oxonium salts with acids.

Derivatives of Dimethylpyrone.

Owing to the ease with which dimethylpyrone hydrochloride appears to become hydrolysed when it is dissolved in water, there seems to be some doubt as to whether its aqueous solution actually contains the true salt of the base or merely a mixture of the base and acid. To throw light on this question, the concentration of the chloride ion has been determined in solutions of different strengths by measuring the potential of the electrode Hg|solid Hg_2Cl_2, solution of dimethylpyrone hydrochloride, against a $N/10$-calomel electrode. Similar measurements were made with various solutions of hydrochloric acid. The equivalent conductivities of all the solutions were also measured, and on plotting the values of the chloridion concentrations as abscissæ against the equivalent conductivities as ordinates, it was found that the curve for dimethylpyrone hydrochloride lies below that for hydrochloric acid, both curves approaching the same value for infinite dilution. From this it is deduced that dimethylpyrone hydrochloride exists in solution as a true salt, although it is hydrolysed to some extent.[9]

Dimethylpyrone forms a large number of additive products with acids, phenols, and nitrophenols.[10] By means of the cryoscopic method, the existence and nature of these substances has been ascertained, and it is found that they may be divided into three classes, having respectively the compositions:

$$C_7H_8O_2,HX \qquad 2C_7H_8O_2,3HX \qquad C_7H_8O_2,2HX$$

The additive compounds are well crystallised, and as a general rule their melting points are lower than those of their components. The reaction between the dimethylpyrone and the other reagent appears to be ionic, and the additive compounds seem to be true oxonium salts.

Some arylidene derivatives of dimethylpyrone[11] have been prepared which form intensely coloured salts with acids. It is concluded that acidic or weakly basic pyrones possess structures containing a bridge formed by the oxygen of the carbonyl group, as suggested by Collie, whilst the arylidenepyrone derivatives are assumed to possess the ordinary unbridged pyrone structure.

Indigo and its Allies.

A considerable amount of work has been carried out on the indigo derivatives, and some reference must be made to the more important branches of this subject.

New syntheses of indigotin[12] have been devised, and methods of preparing substituted indigotins have been studied.[13] It has been shown that experimental conditions have a marked effect on the accuracy of titration of indigotindisulphonic acid with potassium permanganate.[14] The amount of the permanganate required appears to be about 12·6 per cent. less than the theoretical quantity. Efforts have been made to track the source of this error, and it has been found that an addition of manganese sulphate diminishes the difference between theory and practice, whilst the presence of a large excess of sulphuric acid also helps to eliminate the error. Almost theoretical results are obtained when the indigotin solution is added drop by drop to a feebly acid permanganate solution, whilst rapid addition results in too great a quantity of permanganate being used.

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[9] H. N. K. Rørdam, *Oversigt. K. Danske. Vidensk. Selskabs. Forhandl.*, 1914, 243; *A.*, i, 1173.

[10] J. Kendall, *J. Amer. Chem. Soc.*, 1914, **36**, 1222; *A.*, i, 858.

[11] A. A. Boon, K. J. McKenzie, and J. Trotter, *P.*, 1914, **30**, 205; A. A. Boon, F. J. Wilson, and I. M. Heilbron, *T.*, 1914, **105**, 2176.

[12] W. Madelung, *Annalen*, 1914, **405**, 58; *A.*, i, 737.

[13] A. Reissert, *Ber.*, 1914, **47**, 672; *A.*, i, 432; E. Grandmougin and P. Seyder, *ibid.*, 2365; *A.*, i, 1142; H. Levinstein, *J. Soc. Chem. Ind.*, 1914, **33**, 574; *A.*, i, 876; M. Tschilikin, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1834; *A.*, i, 191.

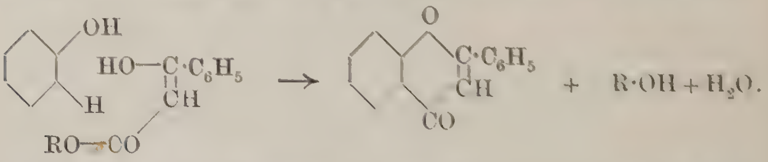
[14] H. E. Wagner, *J. pr. Chem.*, 1914, [ii], **89**, 377; *A.* i, 875.

It has been found that 1-substituted isatins can be obtained by the intramolecular condensation of oxamyl chlorides of the type Cl·CO·CO·NRPh; in some cases the reaction can be brought about by the direct interaction of oxalyl chloride and an amine in the presence of aluminium chloride. Thus oxalyl chloride and ethylaniline produce 1-ethylisatin.[15]

Flavones and Flavonols.

The interaction between phenols and ethyl acetoacetate can follow two very different lines according to the conditions under which it takes place. On the one hand, coumarin derivatives are obtained, whereas if phosphoric oxide is used instead of sulphuric acid the main products are chromones.[16] The latter reaction has now been applied to the preparation of several substances which had previously been synthesised by other methods. In the case of the condensation of resorcinol with methyl methylacetoacetate, no difficulty was experienced in preparing 7-hydroxy-2 : 3-dimethylchromone. When the reaction was carried out with ethyl acetoacetate and phenol, however, no corresponding end-product was obtained. To account for this, it seemed possible that the presence of the phenol had converted the ethyl acetoacetate entirely into the ketonic form, and in order to avoid this, the sodium derivative of ethyl acetoacetate was employed in the reaction instead of the ester itself. The results in this case were normal, a condensation product being readily obtained.

The way was now clear to utilise ethyl benzoylacetate in place of ethyl acetoacetate, and the product of the reaction was flavone:



Thus a new and simple synthesis of this compound has been found, which may in time prove to be a general method for the preparation of various flavone derivatives, whilst alkylated chromones can also be obtained in the same manner from suitable reagents.[17]

On the other hand, the method of synthesis discovered by

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[15] R. Stollé, *Ber.*, 1913, **46**, 3915 ; *A.*, i, 198.

[16] H. Simonis and P. Remmert, *ibid.*, 1914, **47**, 2229 ; *A.*, i, 980.

[17] H. Simonis and C. B. A. Lehmann, *ibid.*, 692 ; *A.*, i, 424.

Auwers and Müller,[18] by which, for instance, the dibromide of benzylidene-4-methylcoumaran-3-one is converted into 6-methylflavonol by treatment with hot alcoholic potassium hydroxide, has been proved[19] to be incapable of general application. It is especially unfortunate that it appears to break down in those cases where the production of naturally occurring flavonols might be expected.

Some work of considerable interest has been carried out in the quercetin group of dyes.[20] These substances in general yield colours which range from yellow to brown, but it seemed possible that, by introducing suitable auxochrome groups into the molecules, a deepening of the tints might be effected which would provide red, violet, or blue colours having the fastness of the original dye.

The choice of the auxochrome groups suitable for producing the required result is not so simple as it appears at first sight. In the alizarin series, the hydroxyl radicle has proved a valuable auxochrome, but its effect in the flavone group does not appear to be so powerful, for there is very little change in tint in passing from luteolin through quercetin to myricetin, although the second compound contains an extra hydroxyl radicle, and the last one has two more hydroxyl groups than are present in luteolin. Nevertheless, the endeavour was made to introduce an additional hydroxyl group into the quercetin molecule, for the possible results extended into more than one field. In the first place, the action of an auxochrome is influenced by its position in the molecular structure, so that it seemed quite likely that if the fresh hydroxyl radicle became attached to the ring in certain positions, it might exert a more marked effect than had been observed in other cases. Further, the synthesis of a new hydroxyquercetin might help to throw light on the structure of the other hydroxyquercetin derivatives such as myricetin, gossypetin, or quercetagin.

The first steps were taken by the complete methylation of the quercetin molecule with a view to protect the hydroxyl radicles in it. Thereafter, the methoxylated substance was nitrated, the nitro-group reduced, and the compound finally demethylated. In this way 6′-aminoquercetin was obtained. Examination of its properties showed that as a dye it did not differ much in tint from quercetin itself, so that the auxochromic action of the amino-group was evidently insufficient to produce the desired result. An attempt was then made to diazotise the amino-compound, but it was not found possible to displace the amino-group by hydroxyl.

A curious point came to light in the course of the investigation.

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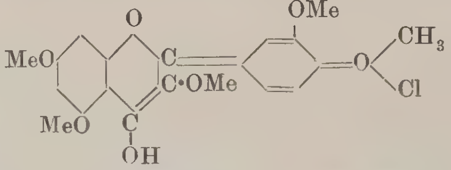
[18] K. v. Auwers and K. Müller, *Ber.*, 1908, **41**, 4233 ; *A.*, 1909, i, 45.

[19] K. v. Auwers and P. Pohl, *Annalen*, 1914, **405**, 243 ; *A.*, i, 981.

[20] E. R. Watson, *T.*, 1914, **105**, 338.

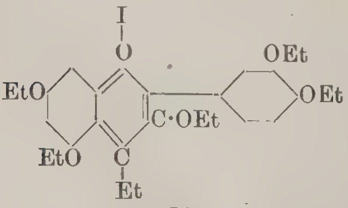
Quercetin itself yields a series of bright yellow oxonium salts, but the progressive introduction of methyl groups appears to render the stability of such salts much less marked. Thus quercetin tetramethyl ether forms only a very unstable sulphate. On the other hand, when a fifth methyl group enters the molecule the power of oxonium-salt formation reappears in full strength, for the pentamethyl derivative of quercetin gives rise to several quite stable salts with mineral acids. These substances are bright yellow, and it seems probable that they have a quinonoid structure of some type such as:



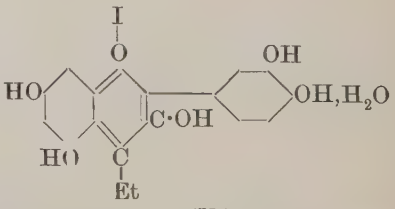
When exposed to air, the salts acquire a surface tint of bright red, for the occurrence of which we have at present no explanation.

The foregoing methods having failed to produce a deeper-coloured dye, various other attempts were carried out.[21] The intermediate compound, 6′-nitroquercetin pentamethyl ether was partly demethylated, yielding 6′-nitroquercetin dimethyl ether; but this was found to be useless for dyeing purposes. Various attempts to introduce additional auxochromes failed, and the multiplication of chromophoric groups in the molecule also gave rise to unsatisfactory results.

Success was attained in another way. The objective sought was to introduce into the molecule some substituent which would produce a permanent quinonoid structure, and this was gained by replacing the pyrone ketonic radicle by the group ·CR·OH. The new compounds of this type might be expected to resemble in behaviour the dyes of the triphenylcarbinol series. Compounds of the following structure (I and II) were therefore prepared by the action of Grignard's reagent on quercetin pentaethyl ether and subsequent de-ethylation with hydriodic acid. The base corresponding with II dyes wool violet or crimson, according as to whether alum or tin is used:



(I.)



(II.)

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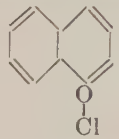
[21] E. R. Watson and K. B. Sen, *T.*, 1914, **105**, 389; compare R. Willstätter and H. Mallison, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 771; *A.*, i, 1081.

Plant Pigments and Allied Materials.

Last year saw the beginning of a systematic investigation of the colouring matters of various flowers, and although the results obtained at first were meagre, they have now been considerably extended. The earliest work dealt with the pigment which gives its colour to the cornflower,[22] and this compound was obtained in a pure, crystalline form, which permitted a chemical investigation of its nature. The results attained tend to show that the anthocyanins, as these pigments are termed, belong to a class of basic vegetable compounds which owe their basicity to an oxygen atom.

The new class of pigments differs from the better known flavone dyes in that the latter form only easily dissociated salts with acids, and therefore do not occur as oxonium salts in the plants from which they are derived; the anthocyanins, on the other hand, can combine with acids to yield comparatively stable oxonium derivatives, somewhat akin to those of phenopyrylium[23]:



An examination of the cornflower pigment, cyanin,[24] has thrown light on the problem of the colour variations which are found in the flowers. Apparently there are three main forms in which the compounds can exist. When combined with mineral acids or the acids of plants, the anthocyanins are red in tint. Neutralisation of the acid causes a change of colour to violet, and it seems probable that the violet type of compound is an internal salt akin to the phenolbetaines, and contains the group:

$$>C-O-O<$$

The addition of alkali produces blue alkali salts, which are to be regarded as derivatives of the neutral violet forms in which no change has been effected in the internal oxonium salt complex.

Thus, what at first sight appear to be three distinct colouring matters are merely modifications of one primary structure under local variations in the distribution of acid and alkali throughout the plant tissues.

The earlier investigations of these pigments led to the proof that the colouring matters are present in the plants in the form of glucosides, so that this chemical class has been found in a hitherto unsuspected field.

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[22] R. Willstätter and A. E. Everest, *Annalen*, 1913, **401**, 189; *A.*, 1913, i, 1371.

[23] H. Decker and T. von Fellenberg, *ibid.*, 1908, **364**, 1; *A.*, 1909, i, 116; compare also H. Decker and P. Becker, *Ber.*, 1914, **47**, 2289; *A.*, i, 1082.

[24] R. Willstätter, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 402; *A.*, i, 564.

Hydrolysis of the pigment of the cornflower leads to its decomposition into two molecules of dextrose and one molecule of the actual colouring matter, which has been termed cyanidin. The latter substance has now been shown to have the composition $C_{15}H_{11}O_6Cl$. The previous estimate of its composition has been found to be erroneous on account of the specimen not having been entirely freed from water, which apparently is very strongly retained by the compound.

The anthocyanin which is present in the rose (*rosa gallica*) is a diglucoside of cyanidin, whilst the pigment of the cranberry is composed of one molecule of galactose combined with one molecule of cyanidin. From this it will be seen that cyanidin is very widely distributed in nature.

Several other anthocyanins have been investigated. Thus grapes owe their colour to the anthocyanin oenin; bilberries are coloured by the compound myrtillin; and, in addition to these, delphinin and pelargonin have been purified.

The methods of extracting the colouring matter naturally vary according to the plant which is used as a starting material, but the essential part of the process is the formation of a sparingly soluble oxonium salt. In the case of grapes, the skins are extracted with glacial acetic acid at the ordinary temperature and the dark red filtrate is precipitated with ether. From the deposit thus obtained a picrate is prepared, and by this means the pigment is purified and the anthocyanin itself obtained. When bilberry skins are worked up, the process is different. The extraction is carried out with a 1 per cent. alcoholic solution of hydrochloric acid; the liquor thus obtained is precipitated with ether, and the pigment is removed from the precipitate by means of water. By the addition of concentrated hydrochloric acid and cooling of the solution, the anthocyanin chloride is precipitated in an almost pure condition.

The investigation of the anthocyanins is rendered difficult by the fact that they are not very stable substances. Aqueous or alcoholic solutions of the pigments gradually lose their colour, in some cases with great rapidity. This alteration in colour does not appear to be due to a reduction of the pigment, but is to be attributed to an isomeric change similar to that which takes place when a triphenylmethane dye is converted into the corresponding carbinol. It has been found that the decolorisation can be delayed by the addition of salts such as sodium chloride, and the addition of excess of mineral acid stops it completely. Further, a cyanidin solution which has become decolorised can be restored to its original condition by the addition of acid.

The absorption spectra of the anthocyanins closely resemble one another; in acid solution they all show a broad absorption band, which extends over the green and blue regions of the spectrum.

Hydrolysis of the anthocyanins produces the corresponding anthocyanidins, which in general resemble each other, although they differ to some extent in crystalline form, solubility, and colour-reaction with ferric chloride. They are much more stable than the parent anthocyanins, for they are apparently not decolorised on keeping in solution. On heating, however, they lose their colour, and this seems to be due to the conversion of the quinonoid pyrone structure of the anthocyanidin into an ordinary pyrone form in which the bridge oxygen has lost its strongly basic properties to a great extent.

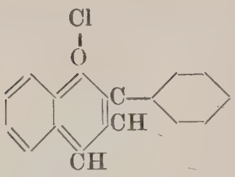
Turning now to the question of the constitution of these substances, a certain amount of information has already been gained. An examination of their empirical formulæ suggests a kinship with the flavone dyes, for the anthocyanidins are isomeric with several substances of the flavone series. Thus cyanidin is isomeric with luteolin and fisetin, pelargonidin is an isomeride of apigenin, whilst delphinidin, quercitin, and morin all have the same molecular composition.

Further relations between the anthocyanidins themselves come to light when we examine the decomposition products which arise from them on heating with alkali.

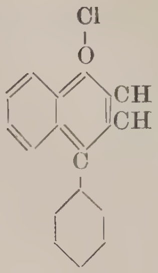
Anthocyanidin	Decomposition Products.
Pelargonidin, $C_{15}H_{10}O_5$	Phloroglucinol and *p*-Hydroxybenzoic acid.
Cyanidin, $C_{15}H_{10}O_6$	,, ,, Protocatechuic acid.
Delphinidin, $C_{15}H_{10}O_7$	,, ,, Gallic acid.

These reactions help to clear up the question of the position of the oxygen atoms in the various anthocyanidin molecules. In the case of pelargonidin, for example, there are five oxygen atoms to account for; three of these are in the phloroglucinol portion, one is in the hydroxyl group of the *p*-hydroxybenzoic acid, a fourth must go to form the pyrone bridge, so that there is only a single oxygen atom left unaccounted for out of the five. Similar reasoning holds for the other substances.

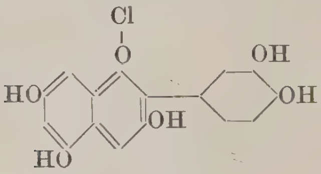
Now when it is recalled that the anthocyanins are apparently pyrylium derivatives there are two possible ways of regarding them; they may be considered as substitution products of either 2-phenylpyrylium or of 4-phenylpyrylium;



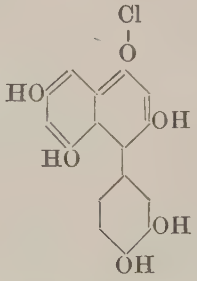
or



On further examination of cyanidin chloride, more light was thrown on the problem. Evidently this substance, on the above assumption, might be either (I) or (II):



(I.)



(II.)

Careful treatment with alkali revealed results which decided the choice.[25] Were (II) the correct formula, it should be possible to isolate as an intermediate product a substituted benzophenone [maclurin, $C_6H_3(OH)_2{\cdot}CO{\cdot}C_6H_2(OH)_3$], but no such substance could be found. Further, formula (I) suggests the possibility that by the oxidation of the anthocyanin a dyestuff of the flavone series might be produced or, conversely, the reduction of a flavone derivative might yield an anthocyanin. The latter process seemed more promising, and quercetin was chosen as a test substance. When reduced in alcoholic solution by means of magnesium and hydrochloric acid in the presence of mercury at 0°, quercetin was found to yield a substance, *allo*cyanidin chloride, which readily loses hydrogen chloride, and is converted into *allo*cyanidin. This resembles closely, but is not identical with, cyanidin. When the reaction is carried out at 35°, however, the end-product is found to be a mixture of *allo*cyanidin and cyanidin itself, the latter synthetic substance being identical with the natural product derived from roses or cornflowers.

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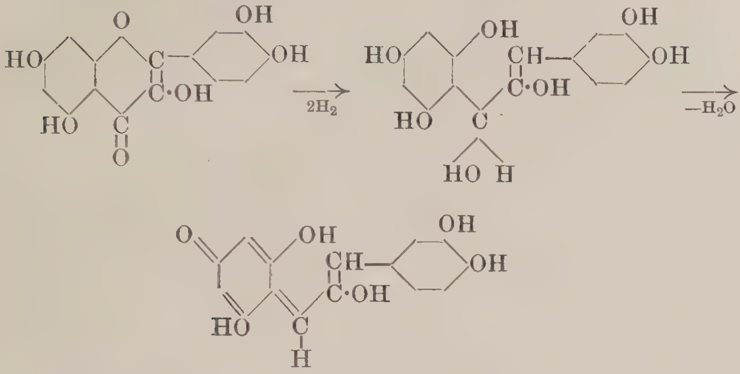
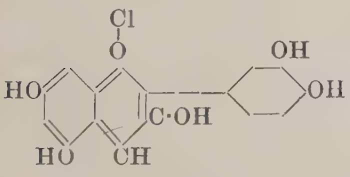
[25] R. Willstätter and H. Mallison, *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 769; *A.*, i, 1081.

According to the views of Willstätter and Mallison, the reduction of quercetin to *allo*cyanidin takes the following course:

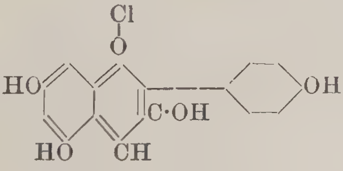


The production of cyanidin itself from quercetin is of the greatest interest from more than one point of view. In the first place, since quercetin itself can be synthesised, the reduction method bridges the gap between the synthetic product and the naturally occurring colouring matter, and a synthesis of the latter has thus been accomplished. Again, this reaction clears up the question of the constitution of the colouring matter, and thus allows us to decide upon probable structural formulæ for the kindred anthocyanidins. It also helps us to trace the relation between the flavone series and the anthocyanins. The anthocyanins in their acid-free forms are isomeric with flavone derivatives which have one atom less of oxygen attached to their benzene nuclei. The flavones and flavonols contain the pyrylium nucleus in an oxidised condition. Thus the relation between members of the two groups is not closest in isomeric compounds, but, instead, we must compare similarly substituted compounds in pairs where the anthocyanin contains an extra atom of oxygen. For example, cyanidin is isomeric with fisetin, but it is closely related to quercetin, as we have seen.

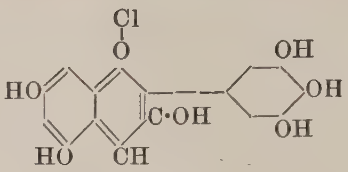
The following structures have been proposed as the best representations of the various chlorides:



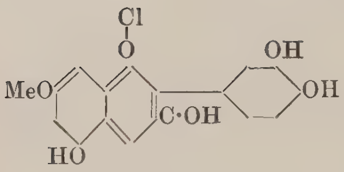
Cyanidin chloride.



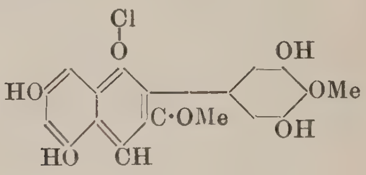
Pelargonidin chloride.



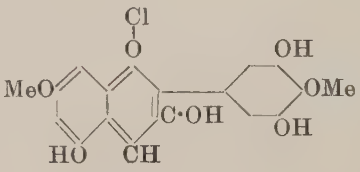
Delphinidin chloride.



Myrtillidin chloride.



Oenidin chloride.



Malvidin chloride.

Various yellow and white flowers have been examined, and from them colouring materials of the anthocyanin group have been obtained by reduction methods.[26] Apparently the reaction gives rise to no anthocyanidin, and if care be taken not to carry the reduction process too far, it is not necessary to reoxidise the product in order to obtain the pigment. This investigation has thrown light upon certain botanical speculations with regard to the production of the anthocyanins from yellow colouring materials.

Willstätter and Mieg's method of extraction has been applied to obtain the fusarium pigment.[27] From *Fusarium orobanchus* two different colouring matters were produced. One of these is a yellow anthocyanin pigment, which is soluble in water or in alcohol at 90°, whilst the other is a red carrotene which resembles that of Willstätter and Mieg in many respects, but differs from it in being more readily soluble in chloroform than in carbon disulphide. The carrotene from fusarium gives the usual colour reactions with acid and alkalis, contains no nitrogen, and crystallises in plates. It has not yet been completely analysed. Solvents have different effects on the colour of the carrotene, according to their nature and the experimental conditions. For example, in cymene the substance forms a reddish-violet solution, but on raising the temperature to the boiling point the colour changes to clear yellow, and as the solution cools again the red tint slowly reappears. Alteration in tint on exposure to air is found in the case of benzene or chloroform solutions of the pigment, where an originally reddish-violet liquid becomes blue.

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[26] A. E. Everest, *Proc. Roy. Soc.*, 1914, [*B*], **87**, 444; *A.*, i, 978.

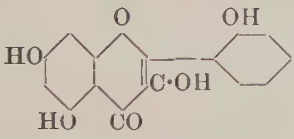
[27] Bezssonoff, *Compt. rend.*, 1914, **159**, 448; *A.*, i, 1135.

The absorption spectra of the three varieties of the carrotene, violet (in boiling alcohol), reddish-violet (in benzene), and yellow (in cymene after boiling), have been examined, and appear to contain three absorption bands, which are shifted in position in passing from the violet to the red compound.

The yellow pigment which occurs along with the carrotene behaves like a weak acid, and easily unites with bases. It appears to be accompanied by sugar, but it has not yet been proved that it is a glucoside.

The roots of *Datisca cannabina* contain varying quantities of two colouring matters; one of these is methoxylated, whilst the second contains no methoxyl group, and has the composition $C_{15}H_{10}O_6$. By benzoylation and acetylation[28] it was shown that four of the oxygen atoms belong to hydroxyl groups, and from the general behaviour of the substance it is deduced that it belongs to the flavone class, being isomeric with fisetin and luteolin.

When hydrolysed with alkali, datiscetin (as the pigment is called) yields salicylic acid, whereas when bromine is employed as a cleavage agent both bromosalicylic acid and tribromophloroglucinol have been identified among the products. These data suggest that datiscetin is probably 1 : 3 : 1′-trihydroxyflavonol,



so that it is very closely allied to morin.

The colouring matter of the blackberry (*Rubus discolor*) has been examined, and several lakes have been prepared from the dye, but so far very little information with regard to its constitution has been obtained.[29]

Crocetin,[30] the pigment of saffron, has been found to have the composition $C_{10}H_{14}O_2$. Various salts of the compound have been prepared and analysed, but in this case, also, our knowledge of the composition of the substance is in an elementary stage.

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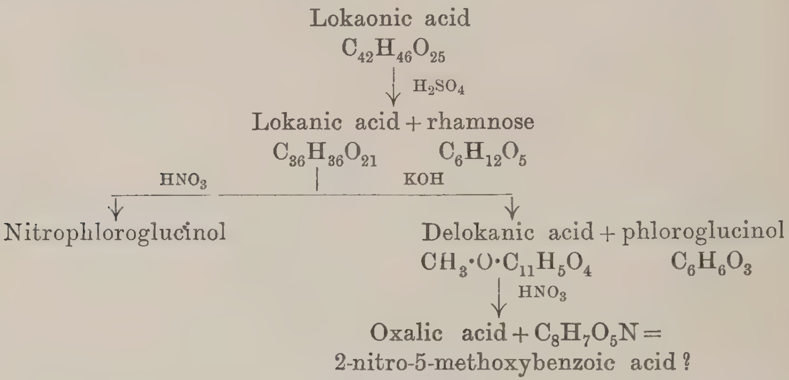
[28] J. Leskiewicz and L. Marchlewski, *Ber.*, 1914, **47**, 1599; *A.*, i, 856.

[29] G. Vecchi, *Staz. sperim. agrar. ital.*, 1914, **47**, 60; *A.*, i, 978.

[30] F. Decker, *Arch. Pharm.*, 1914, **252**, 139; *A.*, i, 979.

The dye lokao, or China green,[31] obtained from *Rhamnus chlorophora*, appears to be much more complex than the other pigments which have recently attracted attention. The ammonium salt (ammonium lokaonate) has the composition $C_{42}H_{45}O_{25}\cdot NH_4$, and, when treated with oxalic acid, liberates lokaonic acid, $C_{42}H_{46}O_{25}$, a bluish-black substance with a metallic lustre. When treated with acids, the ammonium salt decomposes into rhamnose and lokanic acid, $C_{36}H_{36}O_{21}$. The last substance is evidently a phloroglucinol derivative. The following scheme shows some of the decompositions of lokaonic acid and its derivatives:


Lokaonic acid
$C_{42}H_{46}O_{25}$
H_2SO_4
Lokanic acid + rhamnose
$C_{36}H_{36}O_{21}$ $C_6H_{12}O_5$
HNO_3
KOH
Nitrophloroglucinol
Delokanic acid + phloroglucinol
$CH_3\cdot O\cdot C_{11}H_5O_4$ $C_6H_6O_3$
HNO_3
Oxalic acid + $C_8H_7O_5N$ =
2-nitro-5-methoxybenzoic acid ?

Chlorophyll.

In the course of last year, the study of the constitution of chlorophyll advanced rapidly, and the main lines of its structure appear to have been determined with some accuracy. The present year has not seen any great advance in this direction, and most of the work which has been carried out deals with the properties rather than with the constitution of the substance.

It will be recalled that Willstätter's results pointed to the constancy of the chlorophyll quotient in plants; this view has been contested by Borowska and Marchlewski,[32] who state that the quotient varies, not only from species to species, but even in plants of the same species which are subjected to different external conditions. Thus if the absorption spectrum of the pigment is examined, it is found to vary in different plants belonging to the same species, and it is affected even by the stage of growth to which the plant has attained. According to these authors, the absolute and relative amounts of the bluish-green neochlorophyll produced in given cases depend on the character of the soil in which the plant is grown; then, in turn, the quantity of pigment present regulates the power of the plant to absorb light of a suitable wave-length, and this, finally, controls the synthetic processes by means of which the plant tissues are formed.

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[31] A. Rüdiger, *Arch. Pharm.*, 1914, **252**, 165; *A.*, i, 979.

[32] H. Borowska and L. Marchlewski, *Biochem. Zeitsch.*, 1913, **57**, 423; *A.*, i, 73.

Another paper of interest on this question has been published by Stoklasa, Šebor and Senft.[33] According to them, phosphorus enters largely into the processes whereby chlorophyll is produced. They regard chlorophyll as being separable into three different types of compound:

(1) Phæophorbin and its metallic derivatives.
(2) Phæophytin and the phæophytides.
(3) Chlorolecithins of phæophorbinphosphatides.

The third class are compounds of phæophorbin or of phæophorbin with phosphorglycerol. The phosphoric acid is united to the glycerol esters of unsaturated acids or hydroxy-acids. The former acids are produced in the plants during the spring and summer, and are converted into the corresponding hydroxy-acids by oxidation. The change of colour of leaves in autumn depends upon the hydrolytic fission of chlorophyll and the formation of phæophytin and phosphatides, which have a brownish colour, and do not mask the yellow and red tints of the carotins and xanthophyll. Magnesium, calcium, and potassium are the main metallic components of the chlorophyll group, and the first of these is supposed to be an active co-worker with the phosphorus in the growth and metabolism of plants.

The decomposition of chlorophyll in the light and in the dark has been the subject of extensive investigations.[34] When the pigment is exposed to light, aldehydes are liberated, and at the same time a reagent makes its appearance which is capable of decomposing potassium iodide. As is to be expected, the action of light of different wave-lengths is not the same, the red rays having more influence than those of the blue end of the spectrum. Rays of all wave-lengths are active, however, for with a much longer exposure to blue light the same results are obtained as are observed with a short exposure to red rays. The results are similar whether the chlorophyll is bleached in the plant fibre or is extracted and then bleached.

The presence of oxygen is necessary in these photo-decompositions, and the action of the oxygen is evidently not catalytic, as it disappears during the reaction.

Hydrogen peroxide attacks chlorophyll both in the light and in the dark. When light is excluded, the reaction is slower than when the specimen is illuminated. In daylight the reaction does not appear to be much more rapid than the decomposition of chlorophyll in presence of oxygen under the influence of light.

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[33] J. Stoklasa, J. Šebor, and E. Senft, *Bot. Zentr.*, **30**, i, 167; *A.*, i, 423.

[34] H. Wager, *Proc. Roy. Soc.*, 1914, [*B*], **87**, 386; *A.*, i, 561.

The results of these investigations suggest that the production of sugars and starch in the green leaf may not be due to the direct photosynthesis from carbon dioxide in water, but may be brought about by the photo-oxidation of chlorophyll, with the production of aldehyde and a subsequent polymerisation of the aldehyde into sugar.

With regard to the actual mechanism of the photo-oxidation process, it seems probable that hydrogen peroxide plays a part in the reaction. Formaldehyde seems to be a main product in the degradation of chlorophyll.[35] The results obtained in these two series of researches should be carefully collated.

The pigments of brown algæ have been submitted to investigation, and a long-debated question appears to have been settled.[36] Chlorophyll as such has been shown to exist in these plants; and, in addition, there are three yellow, non-nitrogenous pigments: fucoxanthin, carotin, and xanthophyll. The molecular proportion of chlorophyll to the yellow pigments is higher in the land plants than in the algæ.

Phyllocyanin and phylloxanthin have been submitted to further investigation.[37] The former substance was obtained by the action of hydrochloric acid on chlorophyllan, and subsequent purification of the product. On treatment with 1 per cent. aqueous potassium hydroxide, phyllocyanin yields a mixture of anhydrophyllotaonin and some other substance. This paper also contains a criticism of Willstätter's researches on the action of alkalis on chlorophyll.

Pyrrole Derivatives.

The interaction between the Grignard reagent and compounds of the pyrrole group appears still obscure. Two possible views of the mechanism of the reaction have been put forward, one of which presupposes a direct action of the Grignard reagent on a carbon atom of the pyrrole nucleus, whilst the other hypothesis depends upon the assumption that the reaction occurs in two stages, first, an attack upon the imino-group of the pyrrole ring, and then subsequent wandering of the ·MgX group to a point in the nucleus.

An attempt has been made to settle the question by utilising *N*-methylpyrrole as one of the reagents.[38] Here there is no hydrogen atom attached to the nitrogen of the imino-group, so that the "two-stage" process may be left out of consideration. The results in this case are said to be similar to those obtained when pyrroles containing the ·NH· group are used. The work has been criticised, however,[39] on the ground that the *N*-methylpyrrole used was not sufficiently pure, but contained an admixture of unsubstituted pyrrole. It is to be hoped that the matter will be cleared up shortly, as the point is one of some interest.

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[35] C. H. Warner, *Proc. Roy. Soc.*, 1914, [*B*], **87**, 378; *A.*, i, 563.

[36] R. Willstätter and H. J. Page, *Annalen*, 1914, **404**, 237; *A.*, i, 708.

[37] H. Malarski and L. Marchlewski, *Biochem. Zeitsch.*, 1913, **57**, 112; *A.*, i, 72.

[38] K. Hess and F. Wissing, *Ber.*, 1914, **47**, 1416; *A.*, i, 725.

The alkylation of pyrroles has been closely studied recently, and the matter is of importance on account of the relation between the pyrrole group and the colouring matter of the blood. When the Grignard reagent is allowed to act on a secondary pyrrole, the first stage in the reaction appears to be the formation of an *N*-magnesium derivative, and when this is treated with alkyl iodides the product is an alkylpyrrole. Thus, from methyl iodide and magnesium pyrryl bromide it is possible to obtain a mixture of alkyl-substituted pyrroles, of which the most plentiful is 3-methylpyrrole. The reaction appears to be a general one.[40]

The older method of alkylation, by the action of an alkyl iodide on sodium pyrrocarboxylate, has been further investigated in the current year,[41] as well as the direct action of alkyl iodides on pyrroles.[42]

When chloroform is allowed to react with alkyl-substituted pyrroles, the initial step in the process appears to be the elimination of a molecule of hydrogen chloride with the formation of a dichloromethylpyrrolenine. This reaction has been studied in the case of 2 : 3 : 4 : 5-tetrachloropyrrole also,[43] and as it has been found to work with several other pyrrole derivatives, it seems to be a general one.

Another general method applicable in the pyrrole series is the action of sodamide on the dialkylallylacetophenones, the end-products being pyrrole derivatives. Thus, when dimethylallylacetophenone is mixed with its own bulk of benzene and treated with one-fourth of the theoretical amount of sodamide, the chief product appears to be 2 : 4 : 4-trimethyl-5-pyrrolidone.[44]

A third method leading to the synthesis of alkylated pyrroles, namely, the distillation of pyrrolecarboxylic acids, has been the subject of extensive investigation,[45] and numerous methyl derivatives of pyrrole have been produced in this manner.

[39] B. Oddo, *Gazzetta*, 1914, **44**, i, 706 ; *A.*, i, 1142.

[40] B. Oddo and R. Mameli, *ibid.*, 1913, **43**, ii, 504 ; *A.*, i, 80.

[41] *Ibid.*, 1914, **44**, ii, 162 ; *A.*, i, 1142.

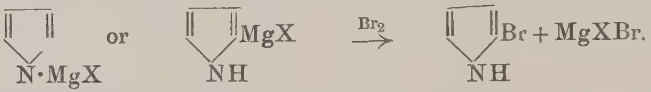
[42] G. Plancher and C. Ravenna, *Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 703 ; *A.*, i, 319.

[43] G. Plancher and T. Zambonini, *ibid.*, 712 ; *A.*, i, 321.

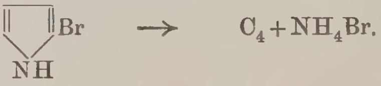
[44] A. Haller and E. Bauer, *Compt. rend.*, 1914, **158**, 1086 ; *A.*, i, 724.

[45] H. Fischer and H. Röse, *Zeitsch. physiol. Chem.*, 1914, **91**, 184 ; *A.*, i, 862.

It is well known that the direct action of halogens on pyrrole derivatives is so violent as to make it impossible to prepare mono-halogen-substituted pyrroles in this manner. A simple method[46] has now been devised by means of which these compounds can easily be obtained. When magnesium methyl iodide is allowed to act on a secondary pyrrole, the hydrogen atom of the imino-group is displaced by the radicle ·Mg·X (where X is a halogen atom). If this compound is treated with halogens at low temperatures, a reaction takes place in accordance with the scheme:



The monohalogen derivatives of pyrrole prepared according to this method are unstable substances, and decompose even on keeping. Thus, bromopyrrole explodes violently when left in a sealed glass tube, the reaction apparently being represented by the equation



During the last twelve months, the study of the indole group has not been pursued with the same vigour as was shown in the previous year. The only point of interest that has arisen is the preparation of 2 : 2′-di-indyl[47] by heating together oxalo-*o*-toluidide and sodium amyloxide at 360°.

Further investigation of the picolide and pyrindole groups have been carried out, and an attempt has been made to determine the influence of substitution on the ease with which the compounds can be prepared.[48] Thus, when β-picoline, γ-picoline, or pyridine itself is heated at 200° with acetic anhydride, no picolide is produced, although members of the picolide group are easily produced from 2 : 4-dimethylpyridine and 6-phenyl-2-methylpyridine under the same conditions.

Pyridine as a Solvent and Catalyst.

The use of pyridine as a solvent for inorganic and organic materials is not new, but some recent work[49] suggests that its application in this capacity requires circumspection before it can safely be regarded as a neutral solvent. When employed in the case of sulphur compounds, it appears to be attended with a certain risk, as the following results show.

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[46] K. Hess and F. Wissing, *Ber.*, 1914, **47**, 1416 ; *A.*, i, 725.

[47] W. Madelung, D.R.-P. 262327 ; *A.*, i, 89.

[48] M. Scholtz, *Arch. Pharm.*, 1913, **251**, 666 ; *A.*, i, 431.

[49] M. Raffo and G. Rossi, *Gazzetta*, 1914, **44**, i, 104 ; *A.*, i, 572.

Sulphur itself dissolves in pyridine on heating, but hydrogen sulphide is liberated, pointing to a decomposition of the solvent. When the solution is allowed to cool, a pitchy material is deposited, which has not yet been fully investigated.

When organic sulphur derivatives are dissolved in pyridine, a similar evolution of hydrogen sulphide takes place, but in this case the hydrogen is not furnished by the pyridine, but is derived from the solute. The pyridine appears to act merely as a catalyst favouring the decomposition of the dissolved substance. Thus, thioacetamide dissolved in pyridine liberates hydrogen sulphide, and becomes converted into acetonitrile; thiobenzamide behaves similarly, and produces benzonitrile.

In the case of diphenylthiocarbamide, the decomposition takes place in two stages. The first phase of the reaction ends in the production of carbodiphenylimide,

$$CS(NHPh)_2 = H_2S + C({:}NPh)_2.$$

As soon as this reaction has run to its conclusion, a second reaction occurs between the carbodiphenylimide and hydrogen sulphide, thus:

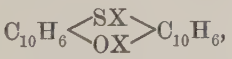
$$3C({:}NPh)_2 + 3H_2S = CS(NHPh)_2 + NH_2Ph + PhN{:}C(NHPh)_2 + CS_2.$$

In the presence of pyridine this reaction proceeds at about 116° (b. p. of pyridine), whereas in the absence of pyridine a temperature 50° higher is necessary in order to bring it about.

Other analogous reactions have been examined, and it appears evident that in the case of sulphur compounds it is necessary to be extremely careful in using pyridine as a solvent on account of these peculiar effects which it produces.

Dinaphthathioxonium Salts.

Reference may be made[50] to the fact that there appear to be two series of salts related to dinaphthathioxin, and it seems not unlikely that they are somewhat akin to the twin series produced from compounds capable of assuming either the phenopyrylium or the ordinary pyrone structure. The thioxonium salts are obtained by the action of an acetyl haloid on naphthasulphonium-quinone or by acting on the corresponding sulphoxide with perchloric or sulphuric acid in hot acetic acid solution. In either of these manners, salts of the following type are formed:



$$C_{10}H_6 < \begin{matrix} SX \\ OX \end{matrix} > C_{10}H_6,$$

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[50] B. Ghosh and S. Smiles, *T.*, 1914, **105**, 1739.

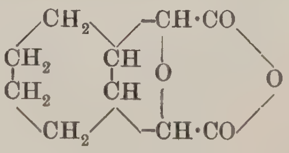
where X represents either a halogen atom or a univalent acid radicle. The true sulphoxide salts are colourless, whereas the thioxonium salts are highly coloured. The perchlorate has been obtained by the use of cold reagents, and, on heating, it is converted into the purple thioxonium perchlorate.

The Alkaloids.

The researches in this department of chemistry during the present year do not appear to have thrown much light on the main problems of alkaloid constitution; steady progress has been made in many directions, but there has been no example of the culmination of an investigation in the case of any of the more important alkaloids. Instead, the researches of the year have been devoted to that clearing up of minor problems which is the necessary preliminary to broader outlooks.

A careful comparison has been made between the properties of quebrachine and those of that interesting alkaloid, yohimbine,[51] and the results seem to establish beyond doubt that the two substances are identical.

A discussion of the present state of our knowledge of cantharidin[52] leads to the conclusion that the formula of this substance is the following:



Cantharidin.

Cantharidin behaves like an anhydride, being gradually neutralised by alkali. When heated with an acetic acid solution of hydrogen bromide, cantharidin gives rise to three products: (1) a dibromo-derivative, to which the structure I is ascribed; (2) a compound, $C_{10}H_{12}O_3Br_2$; and (3) bromohydrocantharic acid, which appears to have the constitution represented by II. The last substance can be resolved into its optically antipodic forms, and when the active forms are reconverted into cantharidin, the synthetic cantharidin is found to be optically inactive, in agreement with the symmetrical structure suggested in the formula above:

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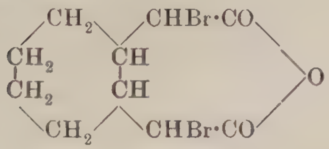
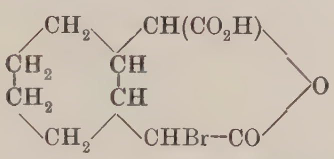
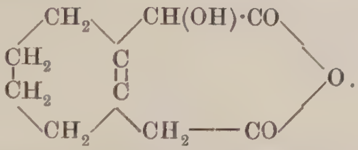
[51] E. Fourneau and H. J. Page, *Bull. Soc. Pharmacol.*, 1914, **21**, 7; *A.*, i, 862.

[52] J. Gadamer, *Verh. Ges. deut. Naturforsch. Aertzte*, 1913 (1914), **2**, 494; *A.*, i, 707.


(I.)


(II.)

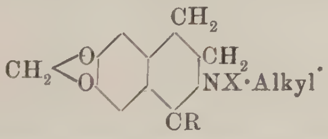
When heated with acetyl chloride, active cantharic acid yields a feebly active substance, *iso*cantharidin, which is assumed to have the following constitution:



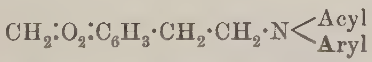
Reference may also be made to the preparation of some saline double compounds from cantharidylethylenediamine.[53]

Metanicotine[54] has been the subject of some investigations during the current year, but as the results do not lend themselves to summarisation, the reader is referred to the original paper.

It has been shown that hydrastinine hydriodide[55] can be prepared by a very simple reaction from dihydrohydrastinine. Alcoholic solutions of iodine and dihydrohydrastinine are mixed in the presence of potassium acetate, and the required compound is obtained from the solution in the usual manner. Various salts of hydrastinine and its homologues[56] have been synthesised, which have structures represented by the following formula, in which R = hydrogen, alkyl, aryl, or alkylaryl; X = acidic group:



In order to prepare them, *N*-acylalkyl derivatives of homopiperonylamine,



$$CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot N{<}^{Acyl}_{Aryl}$$

are condensed with phosphoric oxide, and the dihydro*iso*quinoline derivatives thus obtained are converted into the required salts.

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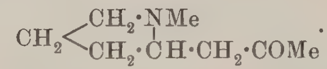
[53] Farbwerke vorm. Meister, Lucius & Brüning, D.R.-P. 269661; *A.*, i, 708.

[54] E. Maass and K. Zablinski, *Ber.*, 1914, **47**, 1164; *A.*, i, 723.

[55] Farbenfabriken vorm. Friedr. Bayer & Co., D.R.-P. 267272; *A.*, i, 79.

[56] H. Decker, D.R.-P. 267699; *A.*, i, 198.

A synthesis of racemic hygrine has been carried out in the following manner.[57] Two isomeric 1-methylpyrrolidylpropanols were prepared, one of which, on oxidation, should yield racemic hygrine. It was found that the use of formaldehyde as a methylating agent resulted in a simultaneous oxidation of the hydroxyl group, and the products were obtained almost quantitatively. Comparison of the synthetic substances with the natural hygrine leads to the conclusion that the latter has the constitution represented by



$$CH_2{<}\begin{matrix}CH_2\cdot NMe\\ CH_2\cdot CH\cdot CH_2\cdot COMe\end{matrix}.$$

The oxidation of hydroxy-amines to amino-ketones, according to the following scheme,

$$\vdots C\cdot NHR\ .\ .\ .\ CH(OH)\ .\ .\ .\ +CH_2O=$$
$$\vdots C\cdot NMeR\ .\ .\ .\ CO\ .\ .\ .\ +H_2O,$$

appears to be of general application.

A considerable amount of work has been done in the tropine group, solanine-*s*[58] having been very carefully examined. The hydrolysis of this compound produces solanidine-*s*, dextrose, *d*-galactose, and *d*-aldomethylpentose. There is thus only one atom of oxygen in the solanidine molecule, and it apparently belongs to a hydroxyl group. The nitrogen atom is present as part of an imino-group in both solanine-*s* and solanidine-*s*.

The action of nitrous acid on amines has been studied in this series of compounds, and the results obtained appear to justify the following conclusions. The primary result of the action of nitrous acid on a primary or secondary amine is the formation of the nitrite, $NHRR',HNO_2$. This compound then undergoes rearrangement into an *as*-dihydroxyhydrazine derivative,

$$NRR'\cdot N(OH)_2.$$

The decomposition of this last substance may follow three lines: (1) *Anazoic decomposition.*—Here nitrogen is evolved, and the results are as follows: ammonium nitrite yields water; primary amines produce water and an alcohol; secondary amines of the type NR_2 decompose, with the formation of a single alcohol, whilst secondary unsymmetrical amines, NRR', give two different alcohols. (2) *Diazoic decomposition.*—Here ammonium nitrite yields nitrosoamine, $NH_2\cdot NO$, or *iso*nitrosoimide, $NH\vdots NOH$; primary amines give either nitrosoamines, $NHR\cdot NO$, or diazohydroxides, $NR\vdots N\cdot OH$, whilst secondary amines form true nitroso-compounds, $NRR'\cdot NO$. (3) *Cyclazoic decomposition.*—In this case, either stable azocyclic compounds or ψ-nitroso-compounds, such as I from aminocamphor nitrite, or *allo*nitroso-compounds like II from ψ-nitroso-oxindole, are obtained:

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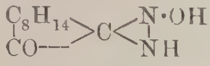
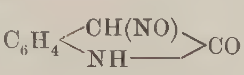
[57] K. Hess, *Ber.*, 1913, **46**, 4104; *A.*, i, 199.

[58] G. Oddo and M. Cesaris, *Gazzetta*, 1914, **44**, ii, 181, 191, 209; *A.*, i, 1173, 1174; F. Tutin and H. W. B. Clewer, *T.*, 1914, **105**, 559.



$$\begin{array}{l}C_8H_{14}\\ |\\ CO\text{---}\end{array}\!>C<\!\begin{array}{l}N\cdot OH\\ \;|\\ NH\end{array}$$

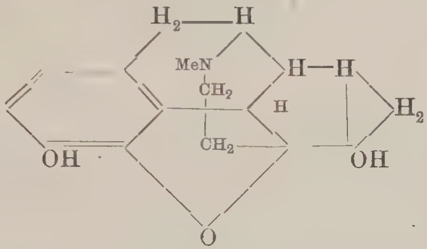
(I.)



$$C_6H_4<\begin{array}{l}CH(NO)\\ NH\text{——}\end{array}>CO$$

(II.)

The following formula for morphine has been proposed by Braun,[59] but the evidence upon which it is based is of so lengthy a nature that it cannot be summarised here, but must be sought in the original paper:



In the group of strychnine alkaloids, progress is being made in our knowledge of decomposition products, but during the present year there is no marked advance along general lines. Strychnine,[60] brucine,[61] acetylbrucinolone,[62] and acetylstrychninolone[63] have all been oxidised by different methods, and the results are likely to aid us later in settling the question of the structure of the various compounds, but it is impossible to give a condensed account of the work in this place.

The addition of bromine to cinchotoxine has been investigated, but the results are of such a detailed character that no purpose would be served in giving a reproduction of them in this place. Here, also, the reader must be referred to the original.[64]

A very complete study of the absorption spectra of various alkaloids belonging to the *iso*quinoline group has been made,[65] and it has been shown that the presence of unreduced catechol nuclei in their molecules introduces a common factor into all the absorption curves. Emetine and cephaeline also show a similar peculiarity, so that it appears probable that their nuclei contain the catechol group, a conclusion which is supported by chemical evidence.

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[59] J. von Braun, *Ber.*, 1914, **47**, 2312; *A.*, i, 1138.

[60] H. Leuchs and G. Schwaebel, *ibid.*, 1913, **46**, 3693; *A.*, i, 79.

[61] H. Leuchs and H. Rauch, *ibid.*, 3917; *A.*, i, 199.

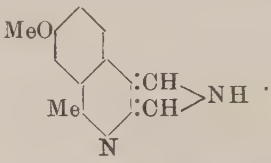
[62] *Ibid.*, 1914, **47**, 370; *A.*, i, 317.

[63] H. Leuchs, *ibid.*, 536; *A.*, i, 429.

[64] G. Rohde and S. Meissner, *ibid.*, 1507; *A.*, i, 719

[65] J. J. Dobbie and J. J. Fox, *T.*, 1914, **105**, 1639.

The constitution of harmine and harmaline still remains in doubt. From the fact that harminic acid yields *iso*nicotinic acid on oxidation, it is concluded[66] that the nitrogen of the pyrrole nucleus cannot be ortho- to the pyridine ring, as a nitropyridinecarboxylic acid might have been expected in that case. Assuming this postulate, which appears to be open to criticism, the following formula for harmine has been suggested by O. Fischer:



The full evidence in favour of it must, however, be looked for in the original paper.

The action of light on mixtures of various alkaloids and ketones[67] has led to some results of interest. When benzophenone is employed along with coniine, sparteine, or piperine, benzopinacone is produced, which is probably formed by the abstraction of hydrogen from the alkaloids. Nicotine condenses with benzophenone, and strychnine appears to be polymerised in the presence of the ketone. Narceine and benzophenone produce a reddish-brown, crystalline substance. Acetophenone with sparteine forms acetophenonepinacone and a gelatinous base.

The Purine Group.

The most important work in this branch of the subject is to be found in some papers by E. Fischer and his colleagues,[68] which apparently mark the opening of another chapter in the history of the synthesis of naturally occurring substances. The objective of the investigations is the synthetic preparation of the nucleotides, but the first steps which have already been taken are concerned with the preparation of glucosides of the purine derivatives. It is hoped that the combination of these glucosides with phosphoric acid will soon be carried out successfully, for this would add the nucleotides to the other three classes, sugars, purines, and polypeptides, for our main knowledge of which we are indebted to Fischer's laboratory. Several of the purine glucosides have now been prepared by the action of acetobromoglucose or its congeners on salts of the purines with silver or other heavy metals. Considerable difficulty has been found in purifying the products, as great care is necessary to prevent hydrolysis taking place. Glucosides of adenine, xanthine, hypoxanthine, guanine, theophylline, and theobromine have been prepared, and in one or two cases galactosides and rhamnosides have also been obtained.

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[66] O. Fischer, *Ber.*, 1914, **47**, 99; *A.*, i, 316; compare *Ann. Report*, 1912, 159.

[67] E. Paternò, *Gazzetta*, 1914, **44**, ii, 99; *A.*, i, 1137.

[68] E. Fischer and B. Helferich, *Ber.*, 1914, **47**, 210; *A.*, i, 333; E. Fischer and K. von Fodor, *ibid.*, 1058; *A.*, i, 741.

Various other papers dealing with the purine group have been published, although they do not lend themselves to detailed description. Thus a series of studies in the degradation of theophylline and its allied compounds has appeared,[69] some uramil derivatives have been examined,[70] and the salt-formation of barbituric acid and its analogues has been investigated.[71]

The Colouring Matter of the Blood.

Last year an account was given of Willstätter's views on the constitution of hæmin,[72] and it appears desirable to summarise here the criticisms which Küster[73] has passed upon them.

Willstätter and Fischer regard the elimination of iron from hæmin as a process which occurs in two stages, the first step being the addition of a halogen hydride to the hæmin molecule, and the next process being the actual removal of iron to produce hæmatoporphyrin. Küster, in his latest publication, objects to this suggestion, and thinks that the matter is better expressed if the addition of halogen hydride and the elimination of the iron atom are regarded as two loosely connected processes which are brought about through the agency of the same reagent.

On Willstätter and Fischer's theory, the metallic atom in the hæmin molecule is united by means of two principal valencies to two pyrrole nitrogen atoms and by two auxiliary valencies to two other nitrogen atoms, each of which is a common member of a pyrrole and a pyridine ring. The action of hydrobromic acid breaks the latter (auxiliary) bonds, leaving the easily ruptured main valencies intact. Küster, on the other hand, brings forward evidence that throws further light on the subject. He finds that when hæmatin is treated under pressure at 130° with 10 per cent. hydrochloric acid, the iron is practically all removed from the molecule, whilst only traces of hæmatoporphyrin are produced; but when hæmin is similarly treated very little iron is displaced, although much hæmatoporphorin is formed. Now it is known that the chlorine in hæmin cannot wholly be removed by the action of alkali, which may be taken as a proof that the non-removable chlorine is attached to a quaternary nitrogen atom, and that the chlorine in hæmin is not united simply with iron or with nitrogen, but must be regarded as standing in some relation to the two elements jointly. This assumed division of the valency of the chlorine atom is regarded by Küster as the cause of the iron atom being able to unite with the basic nitrogen atoms so firmly as to forbid its removal except by the use of energetic reagents.

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[69] H. Biltz and K. Strufe, *Annalen*, 1914, **404**, 131, 137, 170; *A.*, i, 586, 587, 588.

[70] H. Biltz, *ibid.*, 180, 199; *A.*, i, 589, 591.

[71] *Ibid.*, 186; *A.*, i, 590.

[72] *Ann. Report*, 1913, 157–8.

[73] W. Küster, *Zeitsch. physiol. Chem.*, 1913, **88**, 377; *A.*, i, 95.

Küster urges in support of his view that if Willstätter were correct and the chlorine atom played no great part in the matter, then it should be equally easy to remove the iron atom from chlorine-free derivatives of hæmin as it is to eliminate the iron from hæmin itself. This appears, however, to be contrary to the experimental evidence.

Similar views are put forward with regard to the difference in reaction between hæmin and its methyl ester with respect to hydrochloric acid; the dimethyl ester, when thus treated, loses much more iron than does hæmin itself. Küster regards this as a result of the relations subsisting between the carboxyl radicles and the basic nitrogen atoms; the carboxyl and the ferrichloro-groups are supposed mutually to saturate each other's basic properties, and when the dimethyl ester is substituted for the free carboxyl compound, this activity is increased, so that in the dimethyl ester the bond between the chlorine atom and the basic nitrogen atom is weakened to such an extent that the main hold on the iron atom is maintained by the chlorine atom. Whence it follows that the iron in this case becomes more readily separated from the rest of the molecule.

Further evidence is found in the behaviour of mesohæmin, which Küster declares to be lacking in the structural conditions postulated by Willstätter for the stability of its iron atom, although in actual practice the stability of hæmin and mesohæmin do not appear to be very different.

Küster finally objects to Willstätter's rather ex cathedra statement that the existence of a sixteen-membered ring is improbable, and points out that in actual practice such a ring has been obtained by Ruggli.[74]

The paper must, however, be consulted in the original, as it does not lend itself to summarisation.

A general review of the work which has been done on the oxidation of hæmin has been published by Hahn,[75] but it is hardly up to date, for in one section of the subject—the constituent pyrroles of hæmopyrrole oil—the most recent paper mentioned is dated August, 1912.

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[74] P. Ruggli, *Annalen*, 1913, **399**, 174 ; *A.*, 1913, i, 1106.

[75] A. Hahn, *Zeitsch. Biol.*, 1914, **64**, 141 ; *A.*, i, 993.

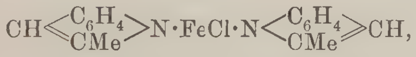
Direct attempts to prepare ferropyrroles[76] have been begun, but the results, so far, have been rather in the nature of clearing the ground. At first it was decided to investigate the reaction between the Grignard reagent and ferric chloride, but the reaction did not seem to promise much when the reagent was prepared from aliphatic derivatives. Thus, magnesium ethyl bromide and ferric chloride yield ethyl chloride, ferrous chloride, and magnesium chlorobromide in accordance with the equation

$$\mathrm{MgEtBr + Fe_2Cl_6 = EtCl + 2FeCl_2 + MgBrCl.}$$

Magnesium phenyl bromide and magnesium benzyl bromide appeared to hold out better hopes, for, although the final products in these cases were respectively diphenyl and dibenzyl, this result points to the intermediate formation of an organo-ferrichloride, which then undergoes decomposition into the hydrocarbon, iron, and ferrous chloride, thus:

$$\mathrm{2FePh_2Cl = C_6H_5Ph + FeCl_2 + Fe.}$$

Success was attained in the preparation of di-2-methylindolyl ferrichloride,



$$\mathrm{CH{<}{\substack{C_6H_4\\CMe}}{>}N{\cdot}FeCl{\cdot}N{<}{\substack{C_6H_4\\CMe}}{>}CH,}$$

which was obtained by the action of ferric chloride on a Grignard reagent derived from 2-methylindole.

When the crude hæmopyrrole of Nencki and Zaleski is treated with diazonium salts, a portion of it produces a red azo-dye, and this particular constituent of the hæmopyrrole mixture has been termed hæmopyrrole I. It has since been shown that this substance is probably 2-methyl-5-ethylpyrrole, and in the present year the matter has been put beyond dispute by the synthesis of the latter compound,[77] which appears to produce the same azo-dye as is obtained from the naturally occurring substance.

The synthetic product is obtained by dry distillation of methylethylmaleinimide with calcium hydroxide and zinc dust in a current of carbon dioxide. When the end-product of this reaction is treated with *p*-toluenediazonium chloride, a mixture of two dyes is obtained, the structures of which are represented by I and II, which concords with the results obtained with the natural hæmopyrrole (I):

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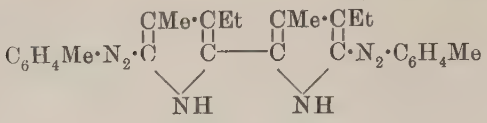
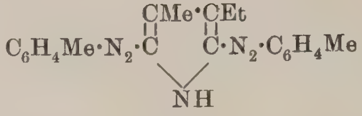
[76] B. Oddo, *Gazzetta*, 1914, **44**, ii, 268; *A.*, i, 1176.

[77] J. Grabowski and L. Marchlewski, *Ber.*, 1914, **47**, 2159; *A.*, i, 993.



(I.)



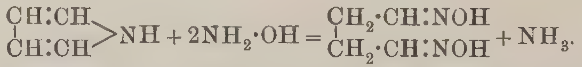
(II.)

The presence of these substances in hæmopyrrole is adduced as evidence that some earlier views will require revision.

The isolation of the constituents of hæmopyrrole oil has been carried out by a process of fractional precipitation with picric acid, and in this way it has been found possible to isolate hæmopyrrole, phyllopyrrole, cryptopyrrole, and the "hæmopyrrole-*a*" of Piloty and Stock.[78]

A separation by means of picrates has also been used in the cases of the esters of phono- and *iso*phono-pyrrolecarboxylic acids.[79] In this way it has been shown that the *iso*phonopyrrolecarboxylic acid obtained from hæmine is identical with that derived from bilirubin.

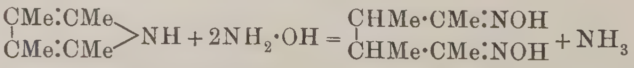
It is well known that when hydroxylamine is allowed to react with pyrrole, the products are ammonia and the dioxime of succinaldehyde:



$$\begin{array}{l}CH{:}CH\\ CH{:}CH\end{array}\!\!>NH + 2NH_2{\cdot}OH = \begin{array}{l}CH_2{\cdot}CH{:}NOH\\ CH_2{\cdot}CH{:}NOH\end{array} + NH_3.$$

Although this reaction is less easy to carry out in the case of the alkyl derivatives of pyrrole, it seemed likely that some interesting results might be obtained in this way in the case of those alkylpyrroles which are connected with the colouring matter of the blood. Attempts have therefore been made in this direction.

Tetramethylpyrrole, when treated with hydroxylamine, is converted into a dioxime of the formula $C_8H_{14}O_2$:



$$\begin{array}{l}CMe{:}CMe\\ CMe{:}CMe\end{array}\!\!>NH + 2NH_2{\cdot}OH = \begin{array}{l}CHMe{\cdot}CMe{:}NOH\\ CHMe{\cdot}CMe{:}NOH\end{array} + NH_3$$

and examination shows that the parent ketone is the same compound as that which is obtained[80] when methyl ethyl ketone is submitted to the action of sunlight.

Bilirubin and hæmin were also treated with hydroxylamine in the hope of producing a fission in their rings, but no results were obtained. On the other hand, porphyrinogen undergoes a reaction totally different from that which was anticipated, for, instead of a rupture of the ring, an oxidation reaction occurs, which yields as end-products mesoporphyrin and ammonia.

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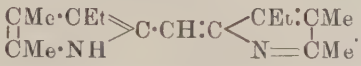
[78] H. Fischer and K. Eismayer, *Ber.*, 1914, **47**, 1820; *A.*, i, 886.

[79] H. Fischer and H. Röse, *ibid.*, 791; *A.*, i, 429.

[80] H. Fischer and W. Zimmermann, *Zeitsch. physiol. Chem.*, 1914, **89**, 163; *A.*, i, 318.

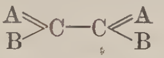
An attempt has been made to prepare coloured derivatives of dipyrrylmethane with a view to a comparison between them and the blood pigment.[81] Substances like the following have been produced by condensing hæmopyrrole-*b* and other compounds with chloroform:



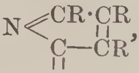
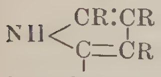
$$\begin{array}{l}\text{CMe}\cdot\text{CEt}\\ \|\\ \text{CMe}\cdot\text{NH}\end{array}\!\!>\text{C}\cdot\text{CH:C}\!<\!\!\begin{array}{l}\text{CEt:CMe}\\ \qquad\quad |\\ \text{N}=\text{CMe}\end{array}.$$

The absorption spectra of the compounds are somewhat similar to that of bilirubin, but do not resemble the spectrum of the colouring matter of the blood.

Similar attempts have been made, using perchloroethane, to produce the twin carbon bridge in compounds of the following type:



$$\begin{array}{c}\text{A}\\ \text{B}\end{array}\!\!>\text{C}-\text{C}\!<\!\!\begin{array}{c}\text{A}\\ \text{B}\end{array}$$

where the radicle "A" is  $\text{N}\!<\!\!\begin{array}{l}\text{CR}\cdot\text{CR}\\ \qquad\ \|\\ \text{C}-\text{CR}\\ \|\end{array}$, and the radicle "B" is  $\text{NH}\!<\!\!\begin{array}{l}\text{CR:CR}\\ \qquad |\\ \text{C}=\text{CR}\\ |\end{array}$. The absorption spectra of the compounds derived from hæmopyrrole-*b* and perchloroethane resemble those of certain chlorophyll derivatives, such as phytochlorin-*e*. Other attempts have been made, using chloral and glyoxal to form bridges, and these also have given rise to products of some interest. Formaldehyde was not found suitable.

The Synthesis of Haematic Acid.

The preparation of hæmatic acid has proved to be comparatively simple.[82] Ethyl α-acetylglutarate was mixed with ether and potassium cyanide, and the calculated quantity of hydrochloric acid was then very gradually added, the reagents being constantly shaken for two days. After separation from by-products, the residue was hydrolysed with 25 per cent. hydrochloric acid, extracted with ether, and the residue, after evaporation, was dissolved in water and shaken with chloroform to remove further by-products. In this way, a mixture of a tricarboxylic acid and a lactone was produced, which, on heating at 183° under 9 mm. pressure, was converted into hæmatic acid. The process is outlined in the following scheme:

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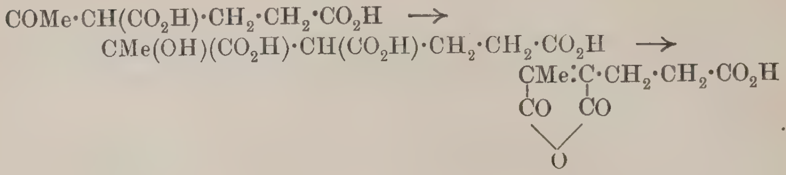
[81] O. Piloty, J. Stock, and E. Dormann, *Ber.*, 1914, **47**, 1124; *A.*, i, 755.

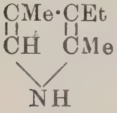
[82] W. Küster and J. Weller, *ibid.*, 532; *A.*, i, 442.



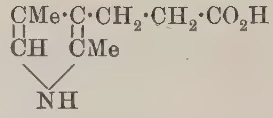
$COMe{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow CMe(OH)(CO_2H){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow$

The Bile Pigment.[83]

As both this subject and its nomenclature are somewhat complicated, it may be well to recall the relations between certain compounds. Hæmatin, which is the non-albuminous component of the blood pigment, forms the source of bilirubin, a constituent of bile. The decomposition of bilirubin produces various substances, among which is bilirubic acid,[84] and this, in its turn, can be degraded to cryptopyrrole and *iso*phonopyrrolecarboxylic acid. Cryptopyrrole has the structure I, whilst for *iso*phonopyrrolecarboxylic acid two alternative formulæ (II and III) have been proposed:

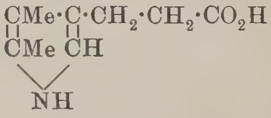


(I.)



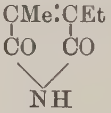
(II.)

or

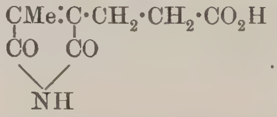


(III.)

When oxidised by another method, bilirubic acid yields different products, methylethylmaleinimide (IV) and hæmatic acid (V):

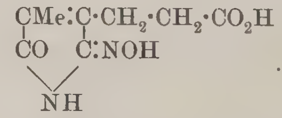


(IV.)



(V.)

Finally, the action of nitrous acid produces methylethylmaleinimide (IV), hæmatic acid (V), and the oxime of phonopyrrolecarboxylic acid (VI), instead of the oxime of the isomeric *iso*phonopyrrolecarboxylic acid:



(VI.)

The same oxime is obtained by the action of nitrous acid on trimethylpyrrolepropionic acid, which seems to show that the propionylcarboxylic acid radicle exerts considerable influence on the structure of the product.

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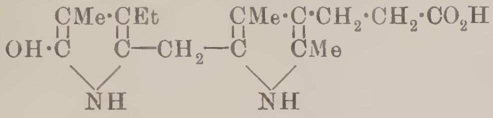
[83] For an account of previous work reference may be made to *Ann. Report*, 1912, 170.

[84] H. Fischer and H. Röse, *Zeitsch. physiol. Chem.*, 1914, **89**, 255; *A.*, i, 309.

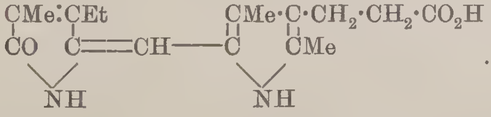
Now, since bilirubic acid, when treated with nitrous acid, does not produce an oxime of its own, but yields, instead, the oxime of phonopyrrolecarboxylic acid (VI), the deduction may be drawn that the "pyrrole acid" in the bilirubic acid molecule is a tetra-substituted one, which leads to the conclusion that the bilirubic acid structure is built up from a trimethylated pyrrolepropionic acid united with the basic pyrrole radicle through substitution of one of the methyl hydrogen atoms by the basic nucleus. In other words, bilirubic acid might have the formula VII:



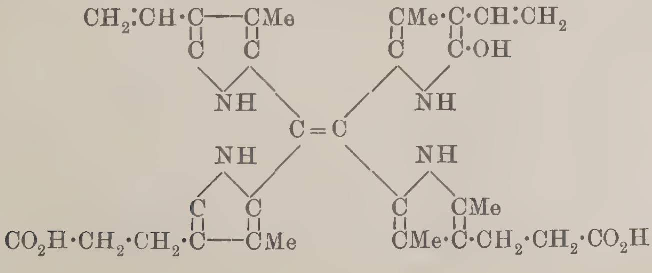
(VII.)

Against this might be urged that sodium ethoxide is almost without action on bilirubic acid, whereas substances containing two pyrrole nuclei united by a methylene group are usually easily decomposed by this reagent. It has now been proved, however, that bilirubic acid (and even hæmin) can be decomposed by means of potassium methoxide, so that this difficulty vanishes, and the proposed formula for bilirubic acid appears to be placed on a sound basis.

The constitution of bilirubin itself now lies open to attack. The action of sodium ethoxide on this substance produces a yellow xanthobilirubic acid, which appears to stand in close relationship with bilirubic acid, since it yields the latter substance on reduction. Its constitution seems to be expressed by



Further considerations drawn from the behaviour of bilirubin and hemibilirubin, into which we cannot enter here, lead Fischer and Röse to the following structural formula for bilirubin:



and in consequence they consider that Willstätter's suggested formula for hæmin is not above discussion.

A comparison between the foregoing Report and those of previous years which covered the same field will show that on the present occasion a greater number of subjects has been dealt with than was the case in 1912 or 1913. This has its advantages in giving an appearance of variety to the Report, but it has the corresponding drawback of leaving in the mind of the reporter a feeling that perhaps he has not devoted sufficient space to certain important fields. It is safe to say, however, that no Report is ever likely to satisfy its author; his chief comfort is based on the hope that his readers may not be so critical of shortcomings as he himself is bound to be. Many subjects have been perforce omitted from the present Report simply because a proper description of them would have entailed too much dwelling upon detail; other subjects have been left out because any full discussion of them would have necessitated somewhat lengthy historical introductions, for which space could not be spared. It must not, therefore, be supposed that the foregoing sections include all the important work of the year: rather should they be regarded as examples of the kind of investigations which are being carried out in the various fields under review.

A. W. STEWART.

ANALYTICAL CHEMISTRY.

The general plan of this Report is identical with that followed in the corresponding Reports of the last three years. The arrangement of the matter falling under the head of organic analysis presents some difficulty, as may be seen by the paragraphs relating to the estimation of sucrose and other carbohydrates being separated by matter cognate to neither. As far as possible, organic methods of general interest are dealt with first, and are followed by short paragraphs dealing with the analysis of foods, drugs, fats, fermentation products, and other materials of special technical interest, but the number of papers referred to under each of these heads is too small to justify cross-headings. Water analysis, not referred to last year, is given a good deal of space, but the separate section on physiological methods is omitted this year, such physiological methods as have been selected for notice finding a natural place elsewhere in the volume.

General.

The solubility, and especially the curve expressing change of solubility with change of temperature, are valuable criteria in deciding the identity of a substance, and also in some cases in deciding whether it is accompanied by impurities, many of which have a marked influence on the solubility. Whereas other physical constants are invariably determined for new substances, concerning many there are no solubility data, or at most a single value for some one temperature. This is, no doubt, partly due to the difficulty attending solubility determinations by the methods generally in use, usually modifications of Noyes' or of Victor Meyer's method. When using Noyes' method, great difficulty is experienced in obtaining accurate results at high temperatures, and although V. Meyer's method gives results of sufficient accuracy, it requires the use of a very large thermostat, which must be maintained constant within 0·1°. A method and apparatus have recently been described which greatly simplify the accurate determination of solubilities at high temperatures. The principle of the method is the determination of solubilities at the boiling point of the saturated solution, the boiling point being varied by changing the pressure. Conducting the determination at the boiling point ensures thorough agitation and eliminates the necessity for using a thermostat, since at constant pressure the boiling point is also constant.[1]

The work of Bingham and his collaborators in improving the means of determining viscosities accurately, yet quickly, and in drawing attention to a fundamental error which vitiated much recent work in this field, was referred to two years ago.[2] In 1912 they described a viscometer with which absolute viscosities could be measured with great certainty. That form of apparatus is easily made, but since its dimensions must be accurately known for absolute measurements, the time consumed in calibration is considerable.[3] For general purposes, it is preferable to calculate the absolute viscosities from measurements that are only relative. By this procedure the calibration is simplified, and the apparatus may be made simpler and less delicate to handle. Many viscometers have been devised for relative measurements, but relative measurements are comparatively useless unless the results can be calculated to absolute units. That measurements obtained by the use of instruments of the Ostwald type could be calculated to absolute units without difficulty has been shown to be an assumption not generally true, this being mainly due to the fact that the formula almost universally used takes no account of the loss of kinetic energy of the liquid within the capillary, this energy disappearing outside the capillary without helping to overcome viscous resistance within it.[4] Viscometers of the ordinary type are deficient, because the pressure producing the flow through the capillary is not variable at will. The result is that, with very fluid substances, the kinetic energy correction becomes large unavoidably, and with rather viscous substances the time of flow becomes intolerably long, necessitating the use of several instruments. With a very long period of flow, the difficulties due to clogging with dust particles become very great.[5] The necessity of the knowledge of the exact density of the liquid at each temperature where a viscosity measurement is desired lessens the convenience of this type of instrument. Both the untrustworthiness and the inconvenience of these instruments may be avoided by using variable pressure, and an instrument working on this principle has now been described which makes it possible to determine the viscosity of any liquid with an error not exceeding 0·1 per cent. For more accurate work, absolute measurements must be made, as data do not exist for standardising a relative instrument for a much higher degree of precision. The instrument is standardised on water at several temperatures, with hexane for very fluid liquids and with sugar solutions for very viscous ones. The instrument is so designed that the correction for kinetic energy is always small, and can therefore be calculated with sufficient accuracy from roughly approximate measurements. Certain minor corrections are necessary, one of them involving the density of the liquid, as does the correction for kinetic energy, but, as both these corrections are very small in a properly proportioned instrument, the density needs only to be known approximately, which constitutes a great advantage of the method.[6]

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[1] L. A. Tschugaev and W. Chlopin, *Zeitsch. anorg. Chem.*, 1914, **86**, 154; *A.*, ii, 348.

[2] *Ann. Report*, 1912, 195.

[3] E. C. Bingham and G. F. White, *Zeitsch. physikal. Chem.*, 1912, **80**, 670; *A.*, 1912, ii, 1144.

[4] E. C. Bingham, *T.*, 1913, **103**, 959.

[5] M. P. Applebey, *ibid.*, 1910, **97**, 2000.

The most useful contributions to microchemical analysis during the year have been two papers dealing with such widely different subjects as elementary analysis of organic substances and the electro-deposition of metals. The latter paper needs to be supplemented by another, which is promised, dealing with such details as current density, time required for complete deposition, and composition of electrolyte; but the apparatus described leaves little to be desired, since it can be easily and cheaply constructed, and serves for the deposition of 0·2 mg. of some metals with an error not exceeding 1 per cent., and that in the presence of 100 times as much of another metal.[7] Methods such as this cannot fail to lead to the adoption of microchemical methods even in cases where there is no lack of material available for analysis, since such methods effect economy, not only of materials, but of the analyst's time, and often, as in this case, of platinum. The author of the other paper cited, which describes and illustrates Pregl's apparatus for micro-elementary analysis, goes so far as to predict that Pregl's methods will become the normal methods of combustion analysis, the results being as exact as those obtained by careful work with larger quantities, whilst the saving of time is very great. Incidentally, this paper describes certain improved absorption tubes and other apparatus, the principles of which may find useful application even in laboratories where it may not be decided to adopt micro-methods.[8]

[6] E. C. Bingham, *J. Ind. Eng. Chem.*, 1914, **6**, 233 ; *A.*, ii, 342.

[7] R. Heinze, *Zeitsch. angew. Chem.*, 1914, **27**, 237 ; *A.*, ii, 482.

[8] J. V. Dubsky, *Chem. Zeit.*, 1914, **38**, 505, 510 ; *A.*, ii, 486.

Gas Analysis.

The iodine pentoxide method for the estimation of carbon monoxide has received much attention this year, one object common to all the authors being reduction of the volume of gas which must be taken for the test. This object is most successfully achieved by Graham and Winmill,[9] who use a 20 c.c. Haldane burette and yet get results accurate to 0·02 per cent. Where the total quantity to be estimated is of the order of 0·1 per cent., a more suitable method is that of Sinnatt and Cramer,[10] which will determine such quantities within about 0·001 per cent. when 2500 c.c. of gas are used in the test. These authors determine, by Pettenköfer's method, the carbon dioxide produced by the oxidation of the carbon monoxide. Their results do not confirm the statement of Seidell[11] and earlier workers that higher and more accurate results are obtainable by determining the iodine liberated from the pentoxide. Each method must be applied with care where the amount of carbon monoxide to be estimated is small, but it is probable that the estimation of the carbon dioxide, using Sinnatt and Cramer's method, offers least difficulty where the concentration to be estimated is of the order stated and the analyst inexperienced in either method. In skilled hands, however, the estimation of the iodine by means of $N/1000$-thiosulphate can be used to determine accurately a much smaller quantity of carbon monoxide.[12] The further statement of Sinnatt and Cramer, that there is no risk of error in conducting the oxidation at 160°, is unfortunate, although, no doubt, true when the carbon dioxide produced, and not the iodine liberated, is determined. That their results by the iodine-titration method were accurate, however, was solely due to the fact that hydrogen was absent from the gas undergoing analysis. Although it is known that hydrogen alone does not react with iodine pentoxide until a much higher temperature than 100° is reached, occasional erratic results have led most users of the iodine pentoxide method to conduct the oxidation at a temperature well below 100°. It has now been shown that, in the presence of carbon monoxide, hydrogen reacts with iodine pentoxide even at 90°, and the exact conditions under which the velocity of reaction can be kept negligibly small, without unduly reducing the temperature and increasing the time required for the oxidation of the carbon monoxide, have been determined.[13] Yellow mercuric oxide, contained in dark glass apparatus, has also been shown to behave like iodine pentoxide as a selective oxidising agent, oxidising carbon monoxide quantitatively, but not attacking methane at 100°.[14]

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[9] J. I. Graham and T. F. Winmill, *T.*, 1914, **105**, 1996.

[10] F. S. Sinnatt and B. J. Cramer, *Analyst*, 1914, **39**, 163; *A.*, ii, 383.

[11] A. Seidell, *J. Ind. Eng. Chem.*, 1914, **6**, 321; *A.*; ii, 489.

[12] G. N. Huntly, *Analyst*, 1914, **39**, 169.

[13] J. I. Graham and T. F. Winmill, *loc. cit.*

A paper on the analysis of complex gas mixtures, issuing from the United States Bureau of Mines, introduces no novel principle, but combines several old ones in such a manner as to increase materially the precision of technical analysis without great loss of speed. In particular, it makes it possible to estimate accurately the hydrogen and paraffins in coal gas, and to determine the mean molecular weight of the paraffins, which may differ so much from that of methane that methods which assume the absence of higher paraffins may underestimate hydrogen by 3 per cent., and overestimate the paraffins (calculated as methane) by a like amount. Carbon dioxide, olefines, and oxygen having been removed in the usual manner, hydrogen and carbon monoxide are oxidised by copper oxide at about 250°, and separately estimated from the contraction due to combustion and further contraction on treatment with potassium hydroxide. The paraffins are then estimated, and their mean molecular weight determined by slow combustion with oxygen, and measurement of the contraction and of the carbon dioxide produced.[15] It has been shown that the simultaneous presence of cerium dioxide, already recommended as a catalyst in ordinary combustion analysis,[16] has the property of greatly increasing the speed of oxidation of hydrogen by copper oxide, whilst it does not bring about the oxidation of methane at 270°.[17]

A recent paper on errors in gas analysis, due to assuming that the molecular volumes of all gases are alike, might have passed unnoticed not many years ago on the ground that the unavoidable errors of experiment—at least in technical gas analysis—were large in proportion to those to which attention is now directed. Technical methods of gas analysis have now, however, been so perfected that refinements in calculation, such as are suggested by the authors of the paper referred to, are fully justified.[18]

Inorganic Analysis.

Qualitative.—Statements in the literature as to the sensitiveness of various reagents for lead being conflicting, experiments have been conducted with a number of such reagents under conditions as nearly as possible identical, and the results tabulated in a useful form.[19] The reaction of copper with 1 : 2-diaminoanthraquinone-3-sulphonic acid, described by Uhlenhuth,[20] is not specific, but is given by nickel and cobalt also. At the same time, it has been found that a simple extension of the test, which is of extraordinary delicacy, suffices to differentiate between these three metals.[21]

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[14] L. Moser and O. Schmid, *Zeitsch. anal. Chem.*, 1914, **53**, 217; *A.*, ii, 384.

[15] G. B. Taylor, *J. Ind. Eng. Chem.*, 1914, **6**, 845; *A.*, ii, 814.

[16] *Ann. Report*, 1913, 178.

[17] J. P. Wibaut, *Chem. Weekblad*, 1914, **11**, 498; *A.*, ii, 585.

[18] G. A. Burrell and F. M. Seibert, *U.S. Bureau of Mines, Technical Paper*, **54**.

A method that will detect aluminium in presence of 1000 times its weight of iron is noteworthy. It depends on the solubility of barium aluminate, and it is not unreasonable to suppose that it might be developed into a method for the approximate estimation of traces of aluminium.[22]

Quantitative.—A new method of estimating bromide in presence of chloride has been based on the fact that, under certain conditions, telluric acid liberates bromine from bromides, but not chlorine from chlorides. The test results show that the method is capable of yielding excellent results, and the authors have been careful to indicate the conditions necessary to success, but, like many other methods due to Gooch, a very slight departure from the conditions laid down may give rise to large errors, and already, in our own Journal, the method has been misdescribed in an essential particular.[23]

In view of the fact that every year slight modifications of old methods for the estimation of phosphoric acid are recommended, modifications which seem to serve no useful purpose, attention may be directed to a recent paper dealing with the Pemberton-Kilgore method, which depends on the precipitation of phosphoric acid as ammonium phosphomolybdate, solution of the washed precipitate in excess of standard alkali, and titration of the excess of alkali, using phenolphthalein as indicator. In spite of many sources of error, the method gives results sufficiently accurate for many purposes if carried out by a chemist accustomed to use it, and saves much time when many determinations have to be made. For occasional work it is likely to prove slower, as well as much less accurate, than the gravimetric (molybdate–magnesia) method. The paper referred to should show any chemist whether the method is one suited to his circumstances. Some fifty cognate papers are cited.[24]

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[19] E. Eegriwe, *Zeitsch. anal. Chem.*, 1914, **53**, 420 ; *A.*, ii, 579.

[20] *Ann. Report*, 1910, 163.

[21] G. Malatesta and E. di Nola, *Boll. Chim. farm.*, 1913, **52**, 819 ; *A.*, ii, 220.

[22] G. H. Petit, *J. Pharm. Chim.*, 1914, [vii], **9**, 66 ; *A.*, ii, 221.

[23] F. A. Gooch and H. I. Cole, *Zeitsch. anorg. Chem.*, 1914, **86**, 401 ; *Amer. J. Sci.*, 1914, [iv], **37**, 257 ; *A.*, ii, 379.

[24] P. L. Hubbard, *J. Ind. Eng. Chem.*, 1913, **5**, 998 ; *A.*, ii, 145.

Several valuable papers dealing with the estimation of silica were published almost simultaneously early in the year. All the authors are agreed that about 1 per cent. of silica is lost if only a single evaporation with acid is made, that repeated evaporation without intermediate filtration is useless, but that all but a negligible trace of the lost silica can be recovered by a single evaporation of the filtrate. This has perhaps been the prevailing view for some years, but it was not universally held. One paper deals with the influence of other acids than hydrochloric acid,[25] whilst another shows that the difficulty in igniting silica to constant weight is not due to the obstinate retention of water, but to the fact that, at the temperature of the blowpipe flame, the solid impurities are slowly volatilised or partly decomposed. The chief impurity is usually sodium chloride, which, so far as it is not volatilised during ignition, is decomposed, with formation of sodium silicate, and it has been proposed that when the silica has been finally treated with hydrofluoric and sulphuric acids, any sodium sulphate remaining should be calculated to sodium oxide, and this amount deducted from the weight of crude "silica."[26] In view of the volatility of sodium chloride, a better course is to treat the silica before ignition with sulphuric acid to decompose chlorides. The weight of the residue then obtained after treatment with hydrofluoric and sulphuric acids is the exact measure of the impurities weighed with the silica.[27]

The determination of silver in bullion, especially bullion high in gold and low in silver, by the cupellation method, is not as satisfactory as might be desired. The silver, being estimated by the difference between the result of the total fine metal assay and the gold assay, bears the errors of both assays, which may not be compensating, and may be large in proportion to the silver present. Thus, differences of 5 fine are common between the results of two laboratories, and even duplicates may differ by this amount, and that on bullion only 100 to 200 fine in silver. Gay Lussac's method has the advantage that, given proper equipment, a large amount of work can be completed daily; but, for accurate work, somewhat elaborate equipment is required, and the method is quite unsuited for occasional work.[28] A preliminary difficulty in applying any wet method to bullion of the character referred to above is the solution of the silver. In view of all these facts, considerable interest attaches to a method which has been, and is still being, investigated in the United States Mint with promising results, although its author is careful to state that many details yet require investigation. The principle of the method is alloying the bullion with cadmium, as suggested a generation ago by Balling,[29] solution of the silver in the alloy by means of nitric acid, and its estimation by Volhard's method.[30]

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[25] M. Wunder and A. Suleimann, *Ann. Chim. anal.*, 1914, **19**, 45; *A.*, ii, 292.

[26] F. A. Gooch, F. C. Reckert, and S. B. Kuzirian, *Zeitsch. anorg. Chem.*, 1914, **85**, 230.

[27] S. B. Kuzirian, *ibid.*, 430; *Amer. J. Sci.*, 1914, [iv], **37**, 61; *A.*, ii, 218.

[28] *Ann. Report*, 1913, 173.

The estimation of silver in colloidal silver preparations and in organic tissue fluids presents some difficulty, which, however, appears to be overcome by two methods recently described.[31]

A method recommended nearly twenty years ago for the separation and estimation of arsenic[32] has been modified, and the modification shown to be of very general application, neither bismuth, cadmium, tin, iron, chromium, nickel, cobalt, manganese, nor zinc interfering. Copper and aluminium in large amounts do interfere, but by a slight modification the method is applicable even to solutions containing much copper. The method depends on the precipitation of the arsenic in the elementary condition by addition of sodium hypophosphite to the hydrochloric acid solution, with filtration of the precipitate and estimation of the arsenic by an iodometric method. The recent modification consists in treating the precipitate with an iodate–iodide mixture. Owing to a trace of free iodine always present, the arsenic dissolves, slowly at first, but more and more rapidly, since iodine is one of the products of the series of reactions which follow the solution of the arsenic. The net result of these reactions is that each atom of arsenic sets free one atom of iodine, and the iodine thus liberated is titrated with thiosulphate.[33] It has been suggested that arsenic may be lost by volatilisation as chloride when following the above method,[34] but this fear is shown to be groundless.[35] For the estimation of small quantities of arsenic in the presence of large quantities of copper, a purpose which the method just described does not fulfil, the method of Avery and Beans[36] can now be confidently recommended. It is far more rapid than any other available method, and depends on the fact that the copper complex formed when an alkali tartrate and alkali hydrogen carbonate are added to

[29] Compare Crookes' "Select Methods of Chemical Analysis," 1886, 443.

[30] F. P. Dewey, *J. Ind. Eng. Chem.*, 1914, **6**, 650, 728; *A.*, ii, 778.

[31] F. Lehmann, *Arch. Pharm.*, 1914, **252**, 9; *A.*, ii, 578; P. W. Danckwortt, *ibid.*, 69; *A.*, ii, 578.

[32] R. Engel and J. Bernard, *Compt. rend.*, 1896, **122**, 390; *A.*, 1896, ii, 448.

[33] L. Brandt, *Chem. Zeit.*, 1913, **37**, 1445, 1471, 1496; *A.*, ii, 68; *ibid.*, 1914, **38**, 461, 474; *A.*, ii, 383.

[34] L. W. Andrews, *ibid.*, 295; *A.*, ii, 291.

[35] L. Brandt, *ibid.*, 295; *A.*, ii, 291.

[36] S. Avery and H. T. Beans, *J. Amer. Chem. Soc.*, 1901, **23**, 485; *A.*, 1901, ii, 623.

a cupric solution is without action on either potassium iodide or iodine.[37]

An entirely novel method of estimating glucinum depends on the fact that basic glucinum acetate is readily sublimed at 160—170°/19 mm., whilst the basic acetates of iron and aluminium are non-volatile in these circumstances.[38] A paper embodying no new principle, but of considerable practical utility, is one dealing with the analysis of commercial aluminium and its light alloys. A primary difficulty in all such work is the separation of the large quantity of aluminium which must be taken in order to get weighable quantities of the minor constituents. By a single operation, the author gets a clean separation of aluminium from everything except tin and nickel, and the preliminary separation of nickel, if present, and the subsequent separation of tin from aluminium, present no difficulty.[39] Some years ago, Brandt proposed the use of diphenylcarbazide as internal indicator in the dichromate titration of iron.[40] The end-point is excellent, but the indicator—of which it is necessary to use an appreciable amount—is itself a reducing agent. The authors who made this observation succeeded in establishing the method on a sound basis.[41] A more recent proposal of Brandt to dispense with a proper correction for the reducing power of the indicator, and to make the method empirical, cannot be endorsed except for routine work on nearly uniform material, but his proof that comparatively large amounts of tervalent arsenic do not interfere is important.[42]

The methods for the separation of iron, aluminium, and chromium from manganese and zinc, based on the fact that the salts of the former group of elements are strongly hydrolysed, whereas those of manganese and zinc are not, or have been supposed not to be, have been studied by means of the ethyl diazoacetate method for estimating the degree of hydrolysis. Solutions of zinc chloride are not perceptibly hydrolysed, but manganese chloride, in millinormal solution at 25°, is said to be hydrolysed to the extent of 10 per cent. It is said to follow from this that acetate separations of manganese from iron can never be sharp, but that the iron precipitate is always contaminated with manganese.[43] Whilst this may be literally true, and thus comforting to those who have failed to acquire skill in acetate separations, the fact

[37] G. D. Lander and J. J. Geake, *Analyst*, 1914, **39**, 116 ; *A.*, ii, 292.

[38] A. Kling and E. Gelin, *Bull. Soc. chim.*, 1914, [iv], **15**, 205 ; *A.*, ii, 295.

[39] R. Belasio, *Ann. Chim. Applicata*, 1914, **1**, 101 ; *A.*, ii, 388.

[40] L. Brandt, *Zeitsch. anal. Chem.*, 1906, **45**, 95 ; *A.*, 1906, ii, 309.

[41] O. L. Barnebey and S. R. Wilson, *J. Amer. Chem. Soc.*, 1913, **35**, 156 ; *A.*, 1913, ii, 248.

[42] L. Brandt, *Zeitsch. anal. Chem.*, 1914, **53**, 1 ; *A.*, ii, 71.

[43] G. van Pelt, *Bull. Soc. chim. Belg.*, 1914, **28**, 101 ; *A.*, ii, 492.

remains that many chemists do make such separations with sufficient sharpness for all practical purposes. That others fail, however, when attempting to follow the directions given by successful users of the method, is sufficient evidence that those directions are incomplete in some essential detail, and the paper under review should be useful to the chemist, who may some day be expected to describe the essential features of this method as successfully as many practise it to-day.

Although manganese is generally estimated to-day by volumetric methods, which leave nothing to be desired in point of accuracy, it is sometimes necessary to separate manganese from other metals, and a recent paper on the conditions which determine the separation of manganese sulphide in the dense green form, which can be easily filtered and washed, should prove useful.[44] A very old method for the estimation of zinc in coinage bronze, which was supposed to have been finally discredited half a century ago, has been revived at the Royal Mint and shown to be as accurate as other available processes, whilst the saving in time is very great. The method consists in volatilising the zinc, while protecting the metal against oxidation. The use of proof assays is necessary, as is a high temperature (1375°), such as was not so readily obtainable in laboratory furnaces at the date when the method fell into disuse.[45]

A new method for the estimation of cobalt in steel depends on the fact that when iron is precipitated by zinc oxide, as in Volhard's method for manganese, but avoiding any unnecessary excess of the reagent, any cobalt (and nickel) present remains in solution, whereas chromium, vanadium, molybdenum, titanium, aluminium, copper, and silica are wholly precipitated. Cobalt is finally separated from nickel and manganese by precipitation with nitroso-β-naphthol in presence of so much hydrochloric acid that nickel is held in solution.[46] Round the dimethylglyoxime method for the estimation of nickel[47] a considerable literature has sprung up, and attention may be called to a summary, by its author, of the more useful suggestions, and a reply to some criticisms which prove to be unfounded.[48]

Owing to the increasing value of platinum–iridium alloys and to the large number of industrial purposes to which these alloys are now being applied, the accurate estimation of iridium is of considerable importance, and attention may be directed to two entirely satisfactory methods which have been reported on under the analytical investigation scheme of the Society of Public Analysts.[49] One of the authors of this report is also partly responsible for some very interesting notes on the differentiation of platinum–iridium and platinum–rhodium alloys, advantage being taken of the fact that, in the presence of small quantities of rhodium, the tendency of silver cupellation leads to spit or vegetate is greatly increased.[50] A useful method for the determination of the purity of platinum ware depends on the fact that the thermoelectromotive force of platinum against many of its alloys has been determined with considerable exactness. Unlike the very exact method depending on measurement of temperature-coefficient of electrical resistance, which is only applicable to wires, the new method can be applied to vessels of any form, and without defacing them.[51]

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[44] A. Villiers, *Compt. rend.*, 1914, **159**, 67 ; *A.*, ii, 658.

[45] T. K. Rose, *J. Soc. Chem. Ind.*, 1914, **33**, 170 ; *A.*, ii, 385.

[46] G. Slawik, *Chem. Zeit.*, 1914, **38**, 514 ; *A.*, ii, 494.

[47] *Ann. Report*, 1907, 205.

[48] O. Brunck, *Zeitsch. angew. Chem.*, 1914, **27**, 315 ; *A.*, ii, 583.

As one of the two rapid methods for the estimation of thorium is not generally available, owing to the fact that the reagent—sodium hypophosphate—cannot be purchased, more importance than would otherwise be the case attaches to a new method which depends on the insolubility of thorium pyrophosphate in dilute acids, the pyrophosphates of the other rare earths, including cerous (but not ceric) cerium, being soluble.[52] It has been observed that when the rare earths are precipitated as hydroxides and ignited to oxides, the results are always somewhat higher, and sometimes much higher, than when they are precipitated as oxalates and ignited. Moreover, the former method gives less concordant results, suggesting the possible formation of basic salts, the amount of which might be expected to vary with the experimental conditions. On the other hand, there was a doubt whether the oxalate precipitation was complete in presence of a trace of mineral acid. This doubt is finally dispelled by a recent research, which shows oxalic acid to be a better precipitant than ammonium oxalate. The latter tends to be carried down as a complex oxalate, which, on washing, is hydrolysed, with the production of rare earth oxalate so finely divided that it passes through the filter. Ammonia does give rise to small quantities of basic salt, but it is only when the hydroxides of the fixed alkalis are used that serious errors are encountered, and these are mainly due to the retention of alkali by the precipitate.[53]

For the estimation of quantities of titanium of the order of

[49] C. O. Bannister and E. A. Du Vergier, *Analyst*, 1914, **39**, 340 ; *A.*, ii, 748.

[50] C. O. Bannister and Patchin, *Inst. Mining and Metallurgy*, 1913, *Bull.* 111.

[51] G. K. Burgess and P. D. Sale, *J. Ind. Eng. Chem.*, 1914, **6**, 452 ; *A.*, ii, 585.

[52] R. J. Carney and E. D. Campbell, *J. Amer. Chem. Soc.*, 1914, **36**, 1134 ; *A.*, ii, 583.

[53] T. O. Smith and C. James, *Chem. News*, 1914, **109**, 219 ; *A.*, ii, 492.

10 mg. with an accuracy of 2 per cent., a method described some years ago in an obscure journal has been subjected to a critical investigation, and shown to be serviceable. It depends on the precipitation of titanium phosphate in acid solution, after reducing iron to the ferrous state.[54] For the more exact separation of larger quantities of titanium and iron, Gooch's method was until recently much used. It depended on precipitation of the iron as sulphide in presence of tartaric acid, which had then to be destroyed before the titanium could be precipitated by the usual reagents. Destruction of the tartaric acid by permanganate, as Gooch directs, generally leads to co-precipitation of manganese when the attempt is made to precipitate the titania by the hydrolysis of the acetate, and a second separation is thus necessitated. This tedious procedure is no longer necessary, since it has been found that Baudisch's reagent (the ammonium salt of nitrosophenylhydroxylamine) will precipitate titanium from solutions containing large quantities of tartaric acid.[55] A similar method serves for the separation of zirconium from iron and aluminium.[56]

Tungsten of more than 99 per cent. purity is now a common object of commerce, and is used in so large a proportion in some high-speed steels that the exact determination of the impurities is important. When the total impurities range from 5 per cent. down to 0·2 per cent., large quantities of metal must be taken for the estimation of the minor constituents, and bringing these large quantities of tungsten into solution introduces a preliminary difficulty. Several alternative methods of bringing the metal into solution are described in a recent paper, which also shows the great variety of impurities that may be present, and how best to estimate each.[57]

Among many papers dealing with the estimation of carbon in steel and iron, attention may be directed to a critical investigation of the comparatively little used method which depends on direct combustion, absorption of the resulting carbon dioxide by means of barium hydroxide, filtration and washing of the precipitated barium carbonate out of contact with air, solution in a measured volume of standard hydrochloric acid, and titration of the excess of acid with alkali. The manipulation of the precipitate requires special apparatus, but this is readily assembled, and the published results show that the method is as exact as the gravimetric methods.

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[54] G. S. Jamieson, *J. Ind. Eng. Chem.*, 1914, **6**, 203; *A.*, ii, 298.

[55] W. M. Thornton, jun. and E. M. Hayden, jun., *Zeitsch. anorg. Chem.*, 1914, **86**, 407; *Amer. J. Sci.*, 1914, [iv], **37**, 407; *A.*, ii, 583.

[56] *Ibid.*, *Chem. News*, 1914, **110**, 153; *Amer. J. Sci.*, 1914, [iv], **38**, 137; *A.*, ii, 779.

[57] H. Arnold, *Zeitsch. anorg. Chem.*, 1914, **88**, 74; *A.*, ii, 679.

Its advantages, as compared with the use of weighed potash bulbs, are obvious, whilst it is not subject to error from access of sulphur trioxide, as is the gravimetric barium carbonate method, which has, nevertheless, found extended adoption.[58]

Electrochemical Analysis.

General interest attaches to new devices which make it possible to conduct electrochemical analysis with a minimum expenditure on platinum apparatus. Attention may be directed to a cheap form of rotating cathode and anode suitable for the rapid estimation of copper and zinc. Not only is it so designed as to reduce the necessary amount of platinum to about 1 gram, but the shape of the anode ensures thorough mixing.[59] Fine-meshed brass gauze has also been shown to be suitable material for the construction of cathodes for the estimation of copper, zinc, and nickel, about 1 gram of platinum wire serving as anode.[60] Tantalum electrodes, recommended two or three years ago,[61] have been stated to become brittle in use[62] and to give unsatisfactory results.[63] It is now shown that they do not become brittle unless relatively high current densities are used, and that the results with tantalum gauze electrodes, now obtainable, are in no way inferior to those obtained with platinum gauze.[64]

It was stated some years ago that copper could be separated from an equal weight of arsenic either from ammoniacal or nitric acid solution.[65] It is now shown that this is only true when the arsenic is present in the arsenic condition,[66] and that it is preferable to work with ammoniacal solutions, as much higher current densities may then be used, and no sensible error is introduced by prolonging the operation long after all the copper has been deposited, in marked contrast to the behaviour of nitric acid solutions.[67] The conditions requisite for the deposition of bismuth in a satisfactorily adherent condition, and for the separation of that metal from arsenic, cadmium, and lead, have now been defined with some precision. The author of this work, in which measurements of cathode potential proved invaluable, suggests that in many cases —once a separation has been shown to be possible and has been studied with the aid of cathode potential measurements—it should be possible to dispense with the elaborate and costly appliances required for measuring cathode potential, and where possible this is certainly desirable.[68]

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[58] J. R. Cain, *J. Ind. Eng. Chem.*, 1914, **6**, 465 ; *A.*, ii, 577.

[59] E. A. Lewis, *J. Soc. Chem. Ind.*, 1914, **33**, 445 ; *A.*, ii, 483.

[60] D. F. Calhane and T. C. Wheaton, *Met. and Chem. Eng.*, 1914, **12**, 87.

[61] O. Brunck, *Chem. Zeit.*, 1912, **36**, 1233 ; *A.*, 1912, ii, 1128.

[62] G. Oesterheld, *Zeitsch. Elektrochem.*, 1913, **19**, 585 ; *A.*, 1913, ii, 823.

[63] G. Wegelin, *Chem. Zeit.*, 1913, **37**, 989 ; *A.*, 1913, ii, 880.

[64] O. Brunck, *ibid.*, 1914, **38**, 565 ; *A.*, ii, 482.

[65] D. S. Ashbrook, *J. Amer. Chem. Soc.*, 1904, **26**, 1285 ; *A.*, 1905, ii, 64.

[66] B. P. Richardson, *Zeitsch. anorg. Chem.*, 1913, **84**, 277 ; *A.*, ii, 148 ; A. Sieverts and W. Wippelmann, *ibid.*, 1914, **87**, 169 ; *A.*, ii, 580.

[67] Sieverts and Wippelmann, *loc. cit.*

The electrolytic reduction of ferric iron as a preliminary to titration with permanganate has been made the subject of study, and it is shown that quantitative reduction can be secured in a few minutes by simple means. Chlorides do not interfere, and a wide range of acidity is permissible.[69]

Attempts have been made to estimate small quantities of alkaloids by an electrochemical method of the type made familiar by the work of Dutoit and Duboux. A solution of the alkaloid containing an excess of hydrochloric acid is titrated with sodium hydroxide solution of known strength, the electrical conductivity of the solution being measured after each small addition. The results when plotted on a system of rectangular co-ordinates give a curve consisting of three well-defined portions, the first representing the neutralisation of the free acid, the second the displacement curve characteristic of the alkaloid, and the third the increase of conductivity due to excess of sodium hydroxide. By comparison with curves obtained with solutions of known composition, small quantities of alkaloids may be estimated.[70]

Organic Analysis.

Experience shows that few qualitative tests sustain the claims made for them. This is particularly the case with tests which are at first claimed to be specific. Tests for which less is claimed, on the other hand, frequently prove useful. Such a one is that which depends on a colour reaction with trichloroacetic acid. So far as the evidence goes, it appears that trichloroacetic acid constitutes, equally with tetranitromethane, a reagent for cyclic double linkings.[71] A test which differentiates between morphine on the one hand and codeine and dionine on the other, and which serves to detect 0·02 mg. of morphine, is deserving of notice, more especially as it has been shown that a dozen or more other common alkaloids do not give a similar reaction.[72] A reaction apparently characteristic of malonic acid and its esters, and certainly not given by acetoacetic and dicarboxyglutaconic esters, depends on the development of an intense blue fluorescence when the substance, in alcoholic solution, is heated with hydrochloric acid, and the mixture then neutralised, mixed with an alcoholic solution of ω-bromomethylfurfuraldehyde, and finally rendered alkaline with alcoholic potassium hydroxide.[73]

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[68] B. P. Richardson, *loc. cit.*

[69] H. C. Allen, *J. Amer. Chem. Soc.*, 1914, **36**, 937 ; *A.*, ii, 581.

[70] R. Goubau, *Bull. Acad. roy. Belg.*, 1914, 63 ; *A.*, ii, 394.

[71] K. V. Charitschkov, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 76 ; *A.*, ii, 390.

[72] T. H. Oliver, *Chem. and Drug.*, 1914, **85**, 249.

For the combustion analysis of organic compounds by Dennstedt's method, a furnace electrically heated internally by means of platinum wires has been designed.[74] A volumetric method has been described for the determination of total carbon in aliphatic substances in the wet way. It is based on oxidation of the substance by potassium dichromate and phosphoric acid to carbon dioxide, or a mixture of carbon dioxide and acetic acid, the carbon dioxide being measured, and the acetic acid distilled from the residual liquid and titrated with baryta. An advantage of the method is the small quantity of the substance required.[75] The direct method for the estimation of oxygen in organic compounds, referred to last year,[76] has been found to give erroneous results when applied to substances of comparatively low oxygen content, but a new method of universal application has now been worked out by the same author. Unfortunately, it is somewhat elaborate, but the value of a direct and exact determination of oxygen is sometimes very great.[77]

A novel method for the estimation of halogens in organic compounds consists in dissolving the substance in alcohol, adding a small quantity of a dilute solution of an alkali hydroxide, and 1—2 grams of calcium carbonate coated with finely divided palladium. The air is displaced by hydrogen, and the reduction completed in a shaking apparatus in an atmosphere of hydrogen under pressure. The halogen is determined by the usual methods in the filtrate from the catalyst, which may be used several times.[78]

Vanadium pentoxide, recommended last year as a catalyst in the absorption of gaseous olefines by sulphuric acid,[79] is now recommended in a similar capacity in Kjeldahl's method of decomposing organic compounds as a preliminary to the estimation of nitrogen.[80] Attention has been called to some limitations of Kjeldahl's method by two physiologists whose work dealt with a number of compounds not covered by Dyer in his report on that process twenty years ago.[81]

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[73] H. J. H. Fenton, *Proc. Camb. Phil. Soc.*, 1914, **17**, 477 ; *A.*, ii, 686.

[74] C. Milchsack and W. A. Roth, *Zeitsch. angew. Chem.*, 1914, **27**, 5 ; *A.*, ii, 147.

[75] E. C. Grey, *T.*, 1914, **105**, 2204.

[76] *Ann. Report*, 1913, 178.

[77] M. C. Boswell, *J. Amer. Chem. Soc.*, 1914, **36**, 127 ; *A.*, ii, 142.

[78] M. Busch, *Zeitsch. angew. Chem.*, 1914, **27**, 432.

[79] *Ann. Report*, 1913, 168.

[80] L. Marino and F. Gonnelli, *Atti R. Accad. Lincei*, 1914, [v], **23**, i, 523 ; *A.*, ii, 575.

The addition of acetic anhydride or of phenol in the estimation of methoxyl by Zeisel's method, as recommended by Herzig and Weishut respectively,[82] has been stated to introduce a source of error, for in the absence of anything but the acetic anhydride or phenol and hydriodic acid, silver iodide may be formed.[83] It has since been shown, however, that the errors thus introduced, although real, are negligible compared with the unavoidable experimental error of the method.[84] The estimation of methoxyl by Zeisel's method in the presence of sulphur compounds is extremely unsatisfactory, on account of the formation of silver sulphide in the absorption flasks. A method has now been devised for the absorption and estimation of the methyl iodide, based on the fact that this substance combines with pyridine, forming pyridine methiodide, which latter may be titrated with silver solution, using sodium chromate as indicator.[85]

A quantitative separation of acetaldehyde and acetone has been based on the fact that the former is quantitatively oxidised by an alkaline silver solution, whilst acetone is scarcely affected.[86] A new method for the estimation of acetone in acetone–water mixtures depends on the fact that two phases separate when sufficient potassium fluoride is added to such mixtures.[87] The method is essentially identical with one previously described for the estimation of alcohol in admixture with water.[88] A gasometric method for the estimation of formic acid depends on the fact that, in the presence of a trace of sulphuric acid, formic acid reacts quantitatively with acetic anhydride, with the production of acetic acid and carbon monoxide.[89]

Mannitol has been estimated hitherto either by the method of Gayon and Dubourg[90] or by that of Muller.[91] The former consists essentially in concentration of the solution until mannitol crystallises, treatment of the magma with a saturated solution of mannitol, followed by filtration, and final extraction of the mannitol from the dry contents of the filter by means of hot alcohol. The limitations of such a method are obvious. Muller's method, depending on the fact that the rotatory power of an aqueous solution of mannitol is notably raised by saturating the solution with borax, is troublesome, since sugars must first be fermented, tartrates and malates removed, and a correction made for glycerol, which, if present, combines with some of the borax and minimises the effect of a fixed quantity of the latter, but it gives excellent results with wines. In the presence of some other substances, such as yeast-water, often employed as nitrogenous food for yeast or bacteria in fermentation experiments, the method fails utterly, and this lends additional importance to a new method which is free from this objection. It is modelled on Wagenaar's method for the estimation of glycerol, and depends on the capacity possessed by polyhydric alcohols of holding cupric hydroxide in solution. The method is invalidated only by the presence of other hexitols.[92] The sugars most commonly found in glucosides, apart from dextrose, are *d*-galactose, *d*-mannose, and members of the methyl pentose group, generally rhamnose, often also rhodeose. Simple pentoses are rarely met with. Dextrose may be characterised by fermentation, galactose is precipitated almost quantitatively by phenylmethylhydrazine, mannose by phenylhydrazine, arabinose by diphenylhydrazine. A recent method for the estimation of rhamnose depends on the formation of a cyanohydrin with hydrocyanic acid, which is easily converted by saponification into α-rhamnohexonic acid (or its lactone), which in turn yields mucic acid on oxidation by nitric acid. The principle of the method might have suggested itself to anyone, but no confidence can be placed in a method depending on oxidation to mucic acid until it has been shown to give constant results. The oxidation of α-rhamnohexonic acid to mucic acid does not appear to be quantitative, but there is a fixed relation between the rhamnose originally present and the weight of mucic acid formed, and this relation is but slightly disturbed by the simultaneous presence of an equal quantity of rhodeose, and in many cases the disturbing influence of rhodeose is negligible, for example, when the purpose in view is the determination of the molecular proportions of a mixture of methyl pentoses, for which an exact method is unnecessary.[93] It has been found that when dilute hydrochloric acid acts on hexoses, starch, and cellulose, ω-hydroxy-5-methyl-2-furfuraldehyde is formed to the extent of 1—2 per cent. Although it is precipitated by phloroglucinol, it does not interfere with the accuracy of pentosan estimations made by the phloroglucinol method, provided aniline acetate is used as indicator. This is accounted for on the ground of the slowness with which the ω-hydroxymethylfurfuraldehyde is produced. The recognition of this substance, however, renders previous estimations of methyl pentosans of doubtful value.[94]

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[81] H. D. Dakin and H. W. Dudley, *J. Biol. Chem.*, 1914, **17**, 275; *A.*, ii, 381.

[82] *Ann. Report*, 1913, 179.

[83] R. J. Manning and M. Nierenstein, *Ber.*, 1913, **46**, 3983; *A.*, ii, 150.

[84] G. Goldschmiedt, *ibid.*, 1914, **47**, 389; *A.*, ii, 223.

[85] A. Kirpal and T. Bühn, *ibid.*, 1084; *A.*, ii, 497.

[86] E. Hägglund, *Zeitsch. anal. Chem.*, 1914, **53**, 433; *A.*, ii, 592.

[87] G. B. Frankforter and L. Cohen, *J. Amer. Chem. Soc.*, 1914, **36**, 1103; *A.*, ii, 548.

[88] *Ann. Report*, 1912, 213.

[89] V. Hottenroth, *Chem. Zeit.*, 1914, **38**, 598; *A.*, ii, 501.

[90] *Ann. Inst. Pasteur*, 1894, **8**, 108.

[91] *Bull. Soc. chim.*, 1894, [iii], **11**, 329, 1073; *A.*, 1894, ii, 141, 334.

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[92] J. Smit, *Zeitsch. anal. Chem.*, 1914, **53**, 473 ; *A.*, ii, 683.

[93] E. Votoček and R. Potměšil, *Bull. Soc. chim.*, 1914, [iv], **15**, 634 ; *A.*, ii, 683.

The formation of a sparingly soluble compound with xanthhydrol has been used for the detection of carbamide in extremely dilute solutions, and its low solubility, together with its high molecular weight—seven times that of carbamide—affords an excellent means for the gravimetric estimation of carbamide by direct precipitation.[95] The gravimetric method possesses the advantage over methods depending on decomposition in the fact that carbamide may at the same time be definitely characterised, and the purity of the derivative confirmed by analysis. When a solution of semicarbazide hydrochloride is treated with potassium chlorate and hydrochloric acid, it is decomposed, with the liberation of exactly two-thirds of its nitrogen in the elementary condition, the remaining third being fixed as ammonium chloride. As carbamide, under similar conditions, is unacted on, the reaction affords a means of estimating semicarbazide in the presence of carbamide.[96]

In applying the double polarisation method to beet molasses, the direct reading is taken in an alkaline solution (owing to the excess of basic lead acetate remaining after clarification), and the inversion reading in an acid medium; the difference between the two observations is not due solely to sucrose, since the rotation of the optically active impurities is modified by the change of reaction to an appreciable extent.[97] In order to avoid this error, it has been proposed to make the direct polarisation in presence of the same amount of citric acid as in the inversion observation, clarification being effected by means of bromine, the excess of which is shown to be without action on the sucrose or invert sugar.[98] The results are about 1 per cent. higher than those obtained by the ordinary procedure involving the direct reading in alkaline solution, but they are substantially identical with those obtained by the improved methods referred to in last year's Report.[98a]

There are still no British data bearing on the cryoscopic method of detecting added water in milk,[99] but the method has been much discussed in Holland,[1] and a single Anglo-Indian writer speaks highly of it.[2]

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[94] Miss M. Cunningham and C. Dorée, *Biochem. J.*, 1914, **8**, 438; *A.*, ii, 783.

[95] R. Fosse, *Compt. rend.*, 1914, **158**, 1076; *A.*, ii, 506.

[96] R. L. Datta, *J. Amer. Chem. Soc.*, 1914, **36**, 1014; *A.*, ii, 504.

[97] *Ann. Report*, 1913, 182.

[98] V. Staněk, *Zeitsch. Zuckerind. Böhm.*, 1914, **38**, 429; *A.*, ii, 586.

[98a] *Ann. Report*, 1913, 182.

[99] *Ibid.*, 1910, 177; 1911, 173; 1912, 214; 1913, 183.

The methods of Lendrich and Nottbohm and of Katz for the estimation of caffeine in coffee are trustworthy, but tedious, and a recent method which gives identical results, and is somewhat quicker, is therefore deserving of notice, although embodying no new principle.[3] A new method for the estimation of nicotine in the presence of ammonia depends on the fact that in alcoholic solution nicotine behaves towards picric acid as a monacid base, whereas in aqueous solution it forms a dipicrate.[4] Until quite recently no method was known for the estimation of strychnine in the presence of quinine with any approach to exactness. A method, which leaves little to be desired in point of accuracy, has now been described, depending on separation of strychnine as ferrocyanide.[5]

Polenske's method of detecting beef fat in lard by the difference between the melting and the solidification points of the fats[6] has been shown to depend mainly on the fact that the α-palmitodistearin of lard has a difference-value greater than 18, whilst the β-palmitodistearin of beef fat has a difference-value of less than 12. The method will detect 15—20 per cent. of beef fat in lard.[7] A recent method, said to be capable of detecting 5—10 per cent., depends on the differences in the melting points of the characteristic glycerides of lard and of beef fat as compared with the melting points of the respective fatty acids. The difference between the melting points of α-palmitodistearin and its separated fatty acids is more than 5°, whilst in the case of β-palmitodistearin the difference is only 0·1°.[8] This method is only a year old, and is not universally approved,[9] but the most recent report on it by authors independent of its inventor, states that 5 per cent. of beef fat can usually be detected, and justifies one in the hope that a real step has at last been taken towards the solution of a very difficult problem.[10]

It has long been known that when to any of the higher fatty acids any other of the higher fatty acids is added in amount up to 20 per cent., the depression of the melting point is proportional to the amount of the added acid, and almost independent of its kind. Advantage is taken of this fact in a method recently proposed for determining the composition of mixtures of the higher fatty acids. For the estimation of palmitic acid, for example, 20 parts of the mixture to be analysed are added to 80 parts of pure palmitic acid, and the melting point is determined. By reference to a table, the percentage of palmitic acid and of acids other than palmitic acid in the final mixture is given, and thus the percentage of palmitic acid, if any, in the mixture to be analysed. Stearic, behenic, and other acids are estimated similarly. Extensions of the method consist in separating the solid fatty acids from a mixture and examining them as described, and also in hydrogenating the original fatty acids by the method of Sabatier and Senderens, and examining the hardened product by the melting-point method. It is possible by methods such as these to show, for example, that the fatty acids of cottonseed oil consist as to 70 per cent. of unsaturated acids with 18 carbon atoms, and as to 25 per cent. of palmitic acid, whilst stearic acid and unsaturated acids with 16 carbon atoms can be shown to be absent.[11]

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[1] *Chem. Weekblad*, 1914, **11**, 126, 198, 201, 204, 206, 207, 209, 323; *A.*, ii, 169, 304, 392.

[2] J. W. Leather, *Analyst.*, 1914, **39**, 432.

[3] G. Fendler and W. Stüber, *Zeitsch. Nahr. Genussm.*, 1914, **28**, 9; *A.*, ii, 757.

[4] R. Spallino, *Gazzetta*, 1913, **43**, ii, 493; *A.*, 1913, ii, 1086.

[5] C. Simmonds, *Analyst*, 1914, **39**, 81; *A.*, ii, 307.

[6] E. Polenske, *Arbeit. a.d. Kaiserl. Gesundheitsamte*, 1907, **26**, 444.

[7] A. Bömer and R. Limprich, *Zeitsch. Nahr. Genussm.*, 1913, **25**, 367; *A.*, 1913, ii, 444.

[8] A. Bömer, *ibid.*, **26**, 559.

[9] K. Fischer and J. Wewerinke, *ibid.*, 1914, **27**, 361.

[10] H. Sprinkmayer and A. Diedrichs, *ibid.*, 571.

A recent method for the estimation of rosin in varnishes, oils, and soaps embodies no new principle, but the tabulated results show that it gives results at least as accurate as any previous method, whilst it is simpler and much more rapid.[12]

The proposal to estimate water in moist alcohol by observing the clouding point of mixtures with other liquids is not new, but none of the methods hitherto based on this principle has proved satisfactory in practice. A recent method of this kind, which makes use of α-bromonaphthalene, a substance readily obtained in a sufficient state of purity for this purpose, makes it easy to determine 1—10 per cent. of water in alcohol within 0·02 per cent.[13]

The method employed for the determination of the original gravity of beer is a purely empirical one, based on the observed relation, in a great number of instances, of the "spirit indication" to the "degrees of gravity lost." It has been known for many years that the table contained in the First Schedule to the Inland Revenue Act, 1880, was seriously inaccurate over an important part of its range, and, in 1909—1911, Sir Edward Thorpe, on behalf of the Treasury, and Dr. H. T. Brown, representing the industry concerned, carried out an investigation with a view to collecting data on which to construct a new table of Original Gravities. This table has just been given Parliamentary sanction,[14] and full details of Thorpe and Brown's work have now been published,[15] whilst at the same time Brown has published a history of previous tables of original gravity, a comparison of these with the new table, and a report on the scientific principles underlying the empirical method of determining original gravity.[16]

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[11] E. Twitchell, *J. Ind. Eng. Chem.*, 1914, **6**, 564; *A.*, ii, 685.

[12] H. Wolff and E. Scholze, *Chem. Zeit.*, 1914, **38**, 369; *A.*, ii, 393.

[13] Miss M. Jones and A. Lapworth, *T.*, 1914, **105**, 1804.

[14] Finance Act, 1914 (Session 2).

Although impossible to summarise in a paragraph, reference must be made to a series of papers on the analysis of mixtures of natural with artificial asphaltum, papers which materially add to our knowledge of the chemistry of asphaltum, and take account of all recent German work on the subject.[17] Their value is to some extent diminished by the fact that the author ignores the work of Clifford Richardson, and indeed of all American writers on this subject.

Agricultural Chemistry.

Since Veitch's method for the estimation of the lime requirement of soils[18] requires at least six independent experiments, and gives much trouble with certain types of soil, an older and simpler method,[19] long since abandoned as misleading, has been modified, and in its new form recommended as giving results substantially identical with those obtained by Veitch's method.[20] Unfortunately, there is already evidence that this is not the case,[21] and until the authors meet the criticism which has been directed against their method, that of Veitch, with all its shortcomings, is likely to be preferred. Admittedly unsatisfactory, Veitch's method has probably been of more service than any other of the many methods described hitherto. The writer will hazard the opinion, however, that it and other methods are destined to give way to a method quite recently described. This method depends on treatment of the soil with $N/50$-calcium hydrogen carbonate, and titration of an aliquot portion of the filtrate. The principle seems unassailable, the technique is of the simplest, and the results are said to be confirmed by pot and field experiments.[21a]

Measuring the capillary lift of soils is not analytical chemistry, but it seems right to call attention here to a recent paper which shows how such measurements can be satisfactorily carried out with apparatus available in most analytical laboratories.[22]

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[15] Sir T. E. Thorpe and H. T. Brown, *J. Inst. Brewing*, 1914, **20**, 569.

[16] H. T. Brown, *ibid.*, 645.

[17] J. Marcusson, *Chem. Zeit.*, 1908, **32**, 965; *Chem. Rev. Fett. Harz-Ind.*, 1911, **18**, 47; *Zeitsch. angew. Chem.*, 1913, **26**, 91; *Chem. Zeit.*, 1914, **38**, 813, 822.

[18] F. P. Veitch, *J. Amer. Chem. Soc.*, 1902, **24**, 1120; *A.*, 1903, ii, 400.

[19] Albert, *Zeitsch. angew. Chem.*, 1888, **1**, 533.

[20] J. A. Bizzell and T. L. Lyon, *J. Ind. Eng. Chem.*, 1913, **5**, 1011; *A.*, ii, 150.

[21] C. R. Moulton and P. F. Trowbridge, *ibid.*, 1914, **6**, 835; *A.*, ii, 828.

[21a] H. B. Hutchinson and K. MacLennan, *Chem. News*, 1914, **110**, 61; *A.*, ii, 784.

[22] C. J. Lynde and H. A. Dupré, *J. Amer. Soc. Agronom.*, 1913, **5**, 107.

Almost the only papers dealing with the analysis of plant material are dated from Rothamsted. Continuing their researches,[23] the workers of this school have determined the cupric reducing power of xylose and arabinose,[24] and have contributed a valuable paper on the estimation of starch. For the estimation of starch in plant materials, the modified Sachsse method, which is official in the United States,[25] and is based on the hydrolysis of starch by means of boiling dilute hydrochloric acid, is quite valueless, not only because such tissues invariably contain pentosans and other substances that yield reducing sugars on hydrolysis, but because of the actual destruction of dextrose which occurs during the prolonged treatment with acid. Although ordinary diastase gives with purified starch results by O'Sullivan's method [26] which are approximately correct, values 15 to 20 per cent. lower than the actual starch content may be obtained when it is applied to leaf material or plant tissues in general, owing to the loss of dextrin which occurs during the purification of the solution by means of basic lead acetate. The observation that basic lead acetate, which does not of itself precipitate dextrin, does carry it down if certain other substances are present, is important to others besides agricultural chemists. For the estimation of starch in plant material, an entirely satisfactory method has been based on Hill's observation [27] that taka-diastase converts starch wholly into maltose and dextrose. The paper includes valuable evidence of the relatively enormous errors that may be introduced in work of this kind unless the greatest care be taken to ensure that the sample taken for analysis is a representative one. In the estimation of starch in dried, ground leaf material, tipping a portion of the sample out of the bottle for analysis, instead of turning the whole sample out, may result in the starch being underestimated by 20 per cent., the heavy starch granules tending to sink to the bottom of the bottle.[28]

The preparation of neutral solutions of ammonium citrate and their use in the analysis of phosphatic manures, which were referred to somewhat fully two years ago,[29] have received much attention during the year under review. As regards the preparation of the solution, it has been shown that a deviation of 0·5 per cent. from the ammonia: citric acid ratio given by Patten and Marti [30] is negligible,[31] whilst a simple method of controlling the hydrion-concentration has been based on colour comparison with a standard solution of hydrochloric acid and disodium hydrogen phosphate, both solutions being tinted with a suitable indicator. The authors of the latter method also make the suggestion that the results of the test would be far less liable to vary if it were agreed to adopt as the standard solution one that was distinctly acid or alkaline, as small differences in the exact composition would then have less influence.[32] Another proposal is the substitution of sodium citrate for ammonium citrate.[33] The preparation of the solution then presents no difficulty, but the results do not always agree with those obtained by the use of ammonium citrate.[34] Most of this work is American, but continental workers have also contributed to the attempt to place this test on a more satisfactory basis.[35]

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[23] *Ann. Report*, 1913, 185.

[24] A. J. Daish, *J. Agric. Sci.*, 1914, **6**, 255.

[25] *U.S. Bureau of Chemistry, Bull.* No. 107.

[26] C. O'Sullivan, *T.*, 1884, **45**, 1.

[27] A. C. Hill, *P.*, 1901, **17**, 184.

[28] W. A. Davis and A. J. Daish, *J. Agric. Sci.*, 1914, **6**, 152 ; *A.*, ii, 588.

[29] *Ann. Report*, 1912, 218.

[30] *Ibid.*, 1913, 185.

[31] P. Rudnick and W. L. Latshaw, *J. Ind. Eng. Chem.*, 1913, **5**, 998 ; *A.*, ii, 145.

Three years ago some space was given to a consideration of methods of analysis of the new nitrogenous fertilisers, and an attempt made to reconcile the conflicting statements made concerning the estimation of cyanamide.[36] A recent paper goes some way in this direction, pointing out that Monnier's results might be explained by polymerisation of a portion of the cyanamide to dicyanodiamide under his experimental conditions. Simple means are described for combating this tendency to polymerisation, whether making use of Caro's[36] or of Kappen's[36] method of analysis, and it is shown that, with this precaution, the two methods give identical results.[37] The accurate estimation of total nitrogen in mixtures of calcium cyanamide and Norwegian nitre was found to present some difficulty, methods which might have been expected to be satisfactory all giving results below the truth. A simple and satisfactory method has now been described.[38]

Water Analysis.

The last two years have witnessed the appearance of an extraordinary number of papers dealing with the estimation of hardness in water, several of them inspired by the comparatively recent method of Blacher, others concerning themselves with the methods devised by Wartha and popularised by Pfeifer about twelve years ago, whilst others either ignore the important work of these authors or attempt to discredit their methods by publishing records of experiments which will not stand examination. Wartha's methods were originally described in a Hungarian journal, of which the present writer has never been able to discover the name; but they were published in German by Pfeifer,[39] and shortly after in English by Proctor,[40] and have given excellent service in many hands during the last ten years. The method for permanent hardness depended on the insolubility of calcium carbonate in the presence of excess of sodium carbonate, and that of magnesium hydroxide in the presence of excess of sodium hydroxide. A volumetric method for estimating magnesia—necessary for calculating the chemicals required for softening purposes—was also based on the insolubility of magnesium hydroxide in presence of excess of calcium hydroxide. A dozen authors might be cited in support of these methods, but a single reference to a recent paper will suffice, more especially as that paper abounds in references and shows that the one author who seriously challenged the accuracy of the method for estimating permanent hardness did not use the Wartha-Pfeifer method at all, but a travesty of it, due to Lunge.[41] The method of Blacher and his co-workers for the estimation of temporary and permanent hardness dates back to 1907,[42] but was not established on a firm basis until last year. In its latest form it depends on titration of the bicarbonate hardness with standard acid, using dimethylaminoazobenzene as indicator, followed by titration of the total hardness with potassium palmitate, using phenolphthalein as indicator. At first potassium stearate was used, but the preparation of the solution was difficult; when made, its titre varied with temperature, owing to separation of solid soap; the end-point left much to be desired, and, in the presence of complex saline mixtures, anomalous results were obtained. These were found to be partly due to the presence of palmitic acid as an impurity in the stearic acid. Pure potassium stearate gave more constant results, but the history of the method as a practical one dates from the adoption of pure potassium palmitate as reagent.[43] Since then the method has been reported on favourably by several independent authors,[44] including

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[32] D. Eastman and J. H. Hildebrand, *J. Ind. Eng. Chem.*, 1914, **6**, 577; *A.*, ii, 675.

[33] A. W. Bosworth, *ibid.*, 227 ; *A.*, ii, 289.

[34] P. Rudnick, W. B. Derby, and W. L. Latshaw, *ibid.*, 486 ; *A.*, ii, 576.

[35] T. Warynski and J. Langel, *Ann. Chim. anal.*, 1914, **19**, 1 ; *A.*, ii, 216.

[36] *Ann. Report*, 1911, 177.

[37] G. Grube and J. Krüger, *Zeitsch. angew. Chem.*, 1914, **27**, 326 ; *A.*, ii, 593.

[38] A. Stutzer, *Chem. Zeit.*, 1914, **38**, 597 ; *A.*, ii, 485.

[39] J. Pfeifer, *Zeitsch. angew. Chem.*, 1902, **15**, 193.

[40] H. R. Proctor, *J. Soc. Chem. Ind.*, 1904, **23**, 8.

[41] J. Zink and F. Hollandt, *Zeitsch. angew. Chem.*, 1914, **27**, 235; *A.*, ii, 490.

[42] C. Blacher, *Rigasche Industrie Zeit.*, 1907, 305; C. Blacher and J. Jacoby, *Chem. Zeit.*, 1908, **32**, 744; *A.*, 1908, ii, 897; C. Blacher, U. Körber, and J. Jacoby, *Zeitsch. angew. Chem.*, 1909, **22**, 967.

[43] C. Blacher, P. Grünberg, and M. Kissa, *Chem. Zeit.*, 1913, **37**, 56; *A.*, 1913, ii, 153.

[44] J. Zink and F. Hollandt, *Zeitsch. angew. Chem.*, 1914, **27**, 437; *A.*, ii, 670; E. Nockmann, *Pharm. Zentr-h.*, 1914, **55**, 435; *A.*, ii, 490; W. Pflanz, *Mitt. Kgl. Landesanst. f. Wasserhyg. zu. Berlin-Dahlem*, 1913, **17**, 141; *A.*, 1913, ii, 1073.

L. W. Winkler, who prefers it to his own method, and makes the useful suggestion that the use of dimethylaminoazobenzene, which is sensitive to carbon dioxide, is best dispensed with, and that the temporary hardness should be estimated by Hehner's original method, using methyl-orange, which is destroyed by means of bromine before proceeding to the titration with potassium palmitate and phenolphthalein. The same author describes an improvement of his method for the estimation of hardness due to lime, depending on titration with potassium oleate, as in Clark's process, using an alkaline tartrate solution to prevent co-precipitation of magnesia.[45] The latter method may prove useful to those who, like one recent author,[46] find difficulty with Wartha's method for magnesia. The writer has instructed many persons in the latter method, all of them acquiring skill in it with ease, and he prefers to estimate magnesia—usually present in least amount—directly, and lime by difference, but the paper referred to cannot be ignored. The use of soap solutions, used in Clark's manner, has tended to fall into abeyance ever since Hehner published his methods for the estimation of hardness, and still more rapidly since Pfeifer published Wartha's method for estimating permanent hardness, which was a great advance on that of Hehner. However, the recent discovery that solutions of potassium myristate, unlike solutions of sodium oleate or of Castile soap, behave similarly towards equivalent solutions of calcium and magnesium, may lead to a revival of Clark's method.[47]

For the estimation of dissolved oxygen in water, Romijn's modification of Winkler's method is in every respect more convenient than the original method, but there are cases where its use may give rise to erroneous results, for example, with sea-water.[48] In these cases, the use of Rochelle salt to inhibit the formation of a precipitate must be abandoned. This involves the abandonment of Romijn's pipette with its manifest advantages. Attention may, therefore, be directed to a new form of pipette for use according to Winkler's original method, but which, like Romijn's pipette, makes it possible to take samples from wells at definite depths or from springs difficult of access, excludes any possibility of error due to atmospheric oxygen, and is convenient to handle.[49] Whilst Winkler's method leaves little to be desired on the score of accuracy, and has been made simpler in execution by the design of apparatus such as that just referred to, circumstances frequently arise where the convenience of a simpler test, that could be completed in the field in a few minutes, would outweigh some small loss of accuracy. The number of simple methods that have been described, some of them too rough to merit consideration, are evidence of a widespread desire for a more satisfactory field method, and attention may therefore be directed to a recent adaptation to field conditions of a method originally due to Linossier, who used phenosafranine as an indicator for ferrous iron in the presence of alkaline tartrate. The field modification of the method is empirical, but in competent hands yields very satisfactory results.[50] The recommendation of the Royal Commission on Sewage Disposal, 1898, that a general statutory standard for effluents can properly be fixed, itself a highly controversial proposition, could find no notice in a report on analytical chemistry if it stood alone, but when the Commissioners in their Eighth Report proceed to formulate a test—the amount of dissolved oxygen taken up from tap-water during five days' incubation—which is unnecessarily troublesome, likely to yield discordant results, and renders useless the analytical data hitherto accumulated, attention must be directed to the test and to the controversy it has aroused.[51]

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[45] L. W. Winkler, *Zeitsch. anal. Chem.*, 1914, **53**, 409; *A.*, ii, 578.

[46] C. Bahlmann, *J. Ind. Eng. Chem.*, 1914, **6**, 209; *A.*, ii, 294.

[47] Miss H. Masters and H. L. Smith, *T.*, 1913, **103**, 992.

[48] W. P. Jorissen, *Zeitsch. anal. Chem.*, 1910, **49**, 424; *A.*, 1910, ii, 749.

[49] J. J. van Eck, *ibid.*, 1913, **52**, 753.

E. B. Phelps suggested the use of an acid solution of *o*-tolidine for the detection of such small quantities of free chlorine as may be present in drinking water which has been treated with hypochlorite. It was recently stated that the method was not adapted to quantitative work,[52] but a slight modification of the original method is now shown to be incomparably the best available for the estimation of quantities of the order of 1 part per million or less.[53] Less than one-hundredth of this amount may be detected by its means, and for some practical purposes its sensitiveness is too great, the comparative bluntness of the starch-iodide reaction having proved to be an actual advantage in devising field methods for use by those engaged in the testing and sterilisation of drinking water for our troops on the Continent.

A recent paper on the estimation of small quantities of lithium in the presence of large quantities of the salts of other metals properly falls into this section. The method substitutes *iso*butyl alcohol for amyl alcohol as a means of separating lithium chloride from the chlorides of sodium and potassium. The latter salts are much less soluble in *iso*butyl alcohol than in amyl alcohol, which is, moreover, objectionable to use. Attention is directed to the fact that, in the course of a water analysis, lithium will usually be underestimated if calcium salts are eliminated in the usual manner, and special methods are described for avoiding such loss of lithium.[54]

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[50] J. Miller, *J. Soc. Chem. Ind.*, 1914, **33**, 185; *A.*, ii, 380.

[51] H. T. Calvert, *ibid.*, 1913, **32**, 265.

[52] Dittoe and Van Buskirk, *Ohio State Board of Health*, 1913, Bull. 3.

[53] J. W. Ellms and S. J. Hauser, *J. Ind. Eng. Chem.*, 1913, **5**, 914; 1914, **6**, 553; *A.*, ii, 66, 669.

At intervals during the last twenty years efforts have been made to agree on a uniform manner of reporting results of water analysis, efforts in which American chemists have been always prominent. Hitherto little has been accomplished, but it is to be hoped that the latest effort of a joint committee of the American Chemical Society, the American Public Health Association, and the Association of Official Agricultural Chemists will be more successful, and lead to similar agreement being reached here. A recent paper discusses the confusion that exists, and advocates reporting the constituents in ionic form.[55] Some at least of the arguments raised against this proposal when it was first made have ceased to have weight.

G. CECIL JONES.

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[54] L. W. Winkler, *Zeitsch. anal. Chem.*, 1913, **52**, 628; *A.*, 1913, ii, 877.

[55] R. B. Dole, *J. Ind. Eng. Chem.*, 1914, **6**, 710; *A.*, ii, 778

PHYSIOLOGICAL CHEMISTRY.

Although the source which usually supplies the bulk of papers dealing with biochemical subjects was cut off when the year had run but little more than half its course, I have not found much relief from the embarrassment with which a plethora of material overtakes the writer of an annual Report. I do not think that it can be fairly said of the contemporary output of work in biochemistry, as is sometimes said by the cynic of the general average scientific output, that a considerable proportion of it can be with advantage neglected. I find, on the whole, very few papers which it is a pleasure to ignore. It is, however, impossible not to feel, just now at any rate, how greatly current American work stands out in significance and importance. The subject has taken firm root on the other side of the Atlantic. It has been appreciated there, and given good equipment. Although a few of the more distinguished workers have been imported, active and successful local schools are making themselves greatly felt. Meanwhile, our own output is increasing satisfactorily, and if one surveys the literature of the year with a mind as little as possible biassed, one really feels that most of those papers which, having read, one wishes to discuss, are just now written in the English language. This applies, it is true, more particularly to the subject of metabolism, but it is studies dealing with metabolism, those concerned with what happens in the animal itself, that mainly justify the specialisation of physiological chemistry. In the case of these Reports, the pure chemistry of physiological substances is naturally often dealt with under the head of Organic Chemistry, whilst the technical methods of the biochemical laboratory receive at least some attention as part of Analytical Chemistry. The chemistry of metabolic processes may therefore legitimately occupy a large part of the more specialised summary. I shall begin this year, however, with a subject which, whilst abstracted under Organic Chemistry, is of special interest to the physical chemist, and perhaps better to be criticised by him. It is, nevertheless, the very legitimate concern of the physiologist,

Catalysis by Enzymes.

Enzyme studies, perhaps as the result of divided responsibility, have been somewhat neglected in these Reports. It would be difficult to give here even the briefest account of the literature that has accumulated since the last reference to the subject; but progress in actual fundamentals is reported in comparatively few papers, and it may be claimed that a large proportion of these is of English or American origin. The significance of this year's work cannot be brought out without a brief discussion of some papers which appeared last year. A communication by W. M. Bayliss[1] dealing with the influence of emulsin on the equilibrium in aqueous solutions of glycerol and dextrose seems especially noteworthy, since the experimental results described remove all foundation for certain statements in the literature which have greatly complicated the whole subject of catalysis by ferments. Particularly important is Bayliss' destructive criticism of the statement that certain reversible reactions require distinct enzymes for catalysis in opposite directions; in other words, that in certain cases enzymes that synthesise have to be distinguished from those which control decomposition. This is a conception which, if it had a sound experimental basis, would clearly remove enzymes from the category of ordinary catalysts. Bayliss shows, further, that, to judge, at any rate, from the case studied by him, an enzyme, when controlling the synthesis of optically active substances, leads to the production of that isomeride which it also decomposes, and not, as has been stated, of its optical antipode. He finds, in fact, that reactions in the system studied follow in all respects the laws deduced from mass-action for equilibrium in a reversible system catalysed by a single enzyme. Closely related to the work of Bayliss is that of E. Bourquelot and his colleagues, who have published during the year many papers dealing with the synthesis of α- and β-glucosides under the influence of appropriate enzymes. The ease with which these biological syntheses are obtained is remarkable. Glucosides were prepared from methyl,[2] ethyl, propyl,[3] and anisyl[4] alcohols; also from glycol, glycerol,[5] and *m*- and *p*-xylene glycols.[6] Methyl[7] and ethyl galactosides[8] were obtained under the influence of an enzyme from bottom yeast. Bourquelot and M. Bridel[9] have studied the equilibrium in a system containing alcohol and dextrose, together with α- and β-glucosidases. The α-ferment induces equilibrium when the ratio of combined and free dextrose is 32·6 to 67·4, whilst with the β-ferment the ratio is 23·39 to 76·61. The authors find that each enzyme is quite without action on the glucoside synthesised by the other, and if both are present the equilibrium proper to each is arrived at independently. The French authors[10] fully confirm, therefore, the observations of Bayliss.

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[1] *J. Physiol*, 1913, **46**, 236; *A.*, 1913, i, 919.

[2] *J. Pharm. Chim.*, 1914, [vii], **9**, 19; *A.*, i, 144.

[3] *Compt. rend.*, 1914, **158**, 70; *A.*, i, 144.

[4] *Ibid.*, 1377; *A.*, i, 706.

[5] *Ibid.*, 1913, **157**, 1024; *A.*, i, 72.

[6] *Ibid.*, 1914, **159**, 213; *A.*, i, 1080.

[7] *Ibid.*, **158**, 204; *A.*, i, 253.

[8] *J. Pharm. Chim.*, 1914, [vii], **9**, 327; *A.*, i, 498.

H. E. and E. F. Armstrong[11] have published, in a most interesting paper, their views concerning the nature of enzymes and enzyme action as based mainly on the results of the long series of experimental researches which they and their co-workers have contributed to the subject. They conclude, as others, and particularly Bayliss, have done, that enzymic action takes place entirely at the surface of colloid particles suspended in the solution of the substrate, and not between substances which are all in true solution. They hold that a hydroclastic enzyme has itself a double function, namely, that of attracting or holding the hydrolyte and that of determining hydrolysis. It is a composite agent in which the functions of a catalyst, such as platinum-black, are combined with those of an acid catalyst. It differs, however, from an ordinary catalyst in displaying a specific and limited activity. Using a nomenclature somewhat akin to that of Ehrlich, they speak of the enzyme as containing an *acceptor*, together with an *agent*. Views as to the possible nature of the acceptor and actor groups in special cases are developed by the authors on characteristically objective lines. With regard to the dynamics of enzyme-controlled reactions, the authors hold that their own experiments confirm the statement, first made by Duclaux in 1898, and subsequently in 1902 by Adrian Brown, and also by Horace Brown and Glendinning, that in each successive interval of time the enzyme determines the hydrolysis of the same amount of substrate. The velocity is thus a linear function of the time, and this relation is held by the Armstrongs to be fundamental, any departure from it being due to the influence of the products of change. The existence of this relation, coupled with the fact that after a certain maximum has been reached increase in the concentration of the hydrolyte diminishes the activity of the enzyme, is held by the authors to show that the laws of mass-action do not apply to enzyme reactions. "In no particular," they write, "is the change 'a mass-action effect,' nor are the departures such that it can be supposed that the change is primarily 'unimolecular,' and subsequently varied owing to the occurrence of secondary changes. . . ."

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[9] *Compt. rend.*, 1914, **158**, 370; *A.*, i, 341.

[10] See for a general discussion of the results obtained, *J. Pharm. Chim.*, 1914, [vii], **9**, 603; *A.*, i, 1147.

[11] *Proc. Roy. Soc.*, 1913, [*B*], **86**, 561; *A.*, i, 1116.

In this view they differ, of course, from most writers who, whilst recognising that the above-mentioned linear time-function is to be frequently observed, consider it as representing only a part of the complete mass-action velocity-curve. It corresponds with certain definite and limited relations between enzyme, substrate, and products in solution. It is true that velocity-curves obtained experimentally have hitherto been fitted by equations derived from considerations of mass-action only by introducing purely empirical constants, but in what is perhaps the most important contribution to our knowledge of enzyme-catalysis published during the present year, D. D. Van Slyke and G. E. Cullen[12] have supplied a mass-action equation covering very exactly the experimental data, and containing no arbitrary constants whatever. The theoretical considerations presented in this paper are based upon an experimental study of the enzyme *urease* obtained from the soja bean. The interest that attaches to this enzyme is clear. It hydrolyses a very simple, neutral, and symmetrical molecule to products of marked chemical activity. It is absolutely specific in relation to its substrate, and controls a reaction of great physiological importance. Its significance has long been recognised by H. E. Armstrong, and as soon as its presence in the soya bean (itself a circumstance of interest) had been demonstrated, in 1909, by Takeuchi, he proceeded to its study and, in conjunction with various co-workers, had established many interesting facts concerning it before the appearance of Van Slyke and Cullen's publications.

For the moment, however, I am concerned with the mass-action formula presented by the latter authors. The form of their equation is based upon the assumption that in a reaction catalysed by an enzyme there are two phases with different velocity-constants, namely, one concerned with the rate of combination of enzyme and substrate, and the other with the rate of the subsequent decomposition. This idea, and the view that it explains why the usual mass-action formula does not hold in zymolysis, were clearly expressed twelve years ago by Adrian Brown. Van Slyke and Cullen, however, justly claim that the whole course of the dual reaction has not hitherto been formulated on these lines in such a way that the assumptions made could be fully tested experimentally.

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[12] *J. Biol. Chem.*, 1914, **19**, 181; *A.*, i, 1181.

Van Slyke's and Cullen's equation takes the form

$$\underbrace{t}_{\text{Time for decomposition of } x \text{ amount of substrate.}} = \underbrace{\frac{1}{E}\Bigl(\frac{1}{c}\log\frac{a}{a-x}}_{\text{Portion of time consumed in uniting enzyme and substrate.}} + \underbrace{\frac{x}{d}\Bigr)}_{\text{Portion of time consumed by enzyme in decomposing substrate.}}$$

a represents the amount of substrate (carbamide) present per unit volume at the beginning of the reaction, x the amount decomposed at time t, E the enzyme concentration, c the velocity of combination of enzyme and substrate, and d the velocity at which the combination splits. It is seen that the ordinary mass-action formula, $t=\frac{1}{K}\log\frac{a}{a-x}$, is only amplified by the addition of a term representing the velocity of the second phase of the dual reaction, but with the result that the equation fits the experimental data with most remarkable accuracy. What is especially important is the circumstance that the two constants involved, c and d, are not arbitrary, but can each be determined experimentally by sufficiently varying the relative velocity of the two distinct phases of the dual reaction. When the concentration of the hydrolyte is sufficiently high (between 0·08 and 10 per cent. of carbamide), even wide variations in the concentration have no effect whatever on the velocity of the reaction, a fact which experiment establishes absolutely. This means that, once such a concentration of substrate is reached, the time spent in uniting enzyme and substrate is negligible. The term $\frac{1}{c}\log\frac{a}{a-x}$, then disappears from the equation, and the value of d can therefore be directly determined. On the other hand, within a range of low concentrations of the hydrolyte, and also under certain other conditions, the ratio c/d becomes relatively small, the time consumed by the first phase of the reaction becomes measurable, and now varies with the concentration of the hydrolyte. Under these conditions, the value of d being known, c can be determined. The experimental data agree so exactly with the calculated values that the assumptions underlying the formula seem to be justified. We have, therefore, an exact expression for the course of an enzyme reaction derived from considerations of mass-action, and also important evidence in favour of its dual nature. Although these results are based upon the study of urease alone, the authors claim, from a study of the available data, that they may be applied to many other ferment-reactions, and probably have a general bearing.

It is interesting to compare Van Slyke's discussion of his results with the expression by the Armstrongs[13] of the view that the laws of mass-action do not apply to enzymes, although the difference is perhaps one of point of view only. When a catalyst forms a temporary compound with the substrate, when that compound is formed with a velocity which is great compared with that of the subsequent decomposition, and when the number of molecules combined with the catalyst (and these alone suffer change) is small compared with the whole number in solution, it is clear that the enzyme-substrate system must remain practically constant in amount, and the rate of decomposition will, so long as the above conditions obtain, be a linear function of the time. We ought not, from any point of view, to expect the ordinary time relations of either a unimolecular or a bimolecular reaction. Only if the linear relations held under all conditions of concentration should we be entitled to wonder what had become of the influence of mass-action. Van Slyke and Cullen's results indicate with exceptional clearness that this is by no means the case, and would seem to justify those who prefer to believe that the normal effects of mass-action, if exerted under somewhat special conditions, are no more in abeyance in enzyme-reactions than elsewhere in chemistry. It should be understood, however, that Van Slyke's clear-cut results and simple formula are obtained only when the influence of the decomposition products is eliminated, a condition that may be easily secured in the case of urease (see below). The work of Van Slyke and Cullen, being directed to other ends, does not take account of the reaction as a balanced reaction, and fails to deal with the question of synthesis as it may occur under the control of the catalyst. The Armstrongs have always given particular attention to the influence of the products of change in their ferment studies. H. E. Armstrong, M. S. Benjamin, and E. Horton[14] have fully investigated their effects in the case of urease, and have brought out, among many other facts, the exceedingly interesting one that the two products of the decomposition of carbamide, namely, ammonia and carbon dioxide, show opposite effects on the course of the reaction, ammonia greatly retarding it, whilst carbon dioxide accelerates it to an equally remarkable extent. Since ammonium carbonate also retards, although to a less degree than ammonia, the action of urease on carbamide is self-inhibitory. Van Slyke and Cullen wholly eliminate this effect by the use of primary and secondary phosphate mixtures, so adjusted that the hydrion-concentration is maintained near the optimum throughout the course of the reaction. In a second paper, Van Slyke, now in conjunction with G. Zacharias, gives a striking account of the influence of hydrion-concentration on the activity of urease. Changes in this have absolutely different and independent effects on the two successive phases of the dual reaction. The combining velocity, represented by c in Van Slyke and Cullen's equation, varies in inverse ratio to the hydrion-concentration, whilst the velocity of decomposition (d in the equation) is greatest at the neutral point, and is retarded by either alkalinity or acidity. Apparently ammonium carbonate inhibits because of its alkalinity, and not specifically, but one feels that the possibility of a synthesis of carbamide from this product of its decomposition under the influence of the enzyme is not negatived by this fact.

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[13] *Loc. cit.*

[14] *Proc. Roy. Soc.*, 1913, [*B*], **86**, 328 ; *A.*, 1913, i, 781.

An important point in Van Slyke and Cullen's work which I have not yet touched upon is the proof, also given by E. K. Marshall,[15] and less fully by Armstrong, that the velocity of the urease reaction is directly and in a linear sense proportional to the enzyme-concentration, and this throughout a wide range. In many cases of enzyme-action the proportionality is said to be not linear, but of a kind that suggests the formation of adsorption compounds between ferment and substrate as a preliminary to the establishment of chemical relations. In the case of urease there is no suggestion of ratios of this sort. The sharply defined maximal amount of carbamide which a given amount of enzyme can hydrolyse per unit time, and the fact that the velocity of hydrolysis is so exactly proportional to the concentration of the enzyme, indicate, in Van Slyke's opinion, the existence of definite combining proportions between catalyst and substrate, and point to more purely chemical relations. We have often, from time to time, been presented with velocity-curves and constants for enzyme-reactions by workers who have taken but little account of the complexity of conditions. Factors of an accidental, or even of an artificial, character have been allowed to intrude into the results. Such results have only been the more misleading because they have received a false and pretentious stamp of accuracy by being presented in mathematical form. The study of enzyme-dynamics, however, seems now to have found itself. Results of real accuracy and significance are being obtained which are important to chemists and biologists alike. Dynamical studies alone, however, will probably fail to tell us all we want to know about ferments. As the Armstrongs very truly remark, in the paper already quoted, it will be difficult to arrive at any final definition of enzymes until their specific nature has been deciphered. We are not at all justified in believing that endeavours to isolate ferments in a pure state, or at any rate in such a form as to offer evidence of constitution, must necessarily fail, but at present we have to be content with speculations. L. Michaelis,[16] it is true, has advanced the view that ferments are substances that undergo electrolytic dissociation in solution, and that the active agent may in one case be the undissociated molecule, and in others the cations or anions respectively. Thus, invertase is an acid of which the undissociated molecules are alone active. Erepsin and lipase are acids which are active only in the form of their anions, whilst pepsin acts proteolytically in the form of cations. These conceptions are founded chiefly upon observations dealing with the effect of varying hydrion-concentrations on the activity of the enzymes, and on the direction of their migration when submitted to a potential gradient. The facts are interesting; but it is doubtful if the experimental evidence can bear the weight of the conclusions, and, in any case, it does not throw much light upon the actual chemical nature of enzymes. The Armstrongs postulate that the relation of the "acceptor section" of the enzyme to the hydrolyte is not that of key and lock in Emil Fischer's sense, "but that of a superposable, and therefore identical, radicle." The "agent" section which promotes hydrolysis is possibly a carboxyl group acting under exceptionally favourable conditions. These views are suggestive, but they remain, of course, purely speculative. Investigations such as those of J. M. Nelson and S. Born[17] into the "constitution" of invertase will scarcely be accepted as having arrived at a demonstration of the nature of a ferment, and I imagine that few at present will find much sympathy with the view of Barendrecht[18] that "an enzyme particle contains the same molecule [as that] which is liberated or acted upon by this enzyme, in some active state," the activity spreading through the solution of substrate as a radiation.

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[15] *J. Biol. Chem.*, 1914, **17**, 351 ; *A.*, i, 606.

If ever we arrive at a knowledge of the chemical constitution of enzymes, we shall learn a great deal more than we now know about the constitution of the living cell.

The view that zymolysis depends upon the preliminary formation of a compound between substrate and catalyst underlies much of the work of L. Michaelis. To this belief, indeed, all authors are coming, and the conception of "contact" catalysis is disappearing from the field of enzyme chemistry. Michaelis and his co-workers have been studying the action of substances which inhibit zymolysis. It is assumed that inhibitors can act in one of two ways:

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[16] *Biochem. Zeitsch.*, 1913, **49**, 333; *A.*, 1913, i, 540; *ibid.*, 1914, **60**, 43; *A.*, i, 443; *ibid.*, 1914, **65**, 1; *A.*, i, 1007.

[17] *J. Amer. Chem. Soc.*, 1914, **36**, 393; *A.*, i, 339.

[18] *Biochem. J.*, 1913, **7**, 549; *A.*, i, 214.

they can either (*a*) combine with the ferment, or (*b*) diminish the rate of decomposition of the substrate-ferment compound.

L. Michaelis and P. Rona[19] have developed in theory and practice a method for determining which of these alternatives may hold in a given case, and find, to take one instance, that, in the case of yeast-maltase, sodium chloride, sodium nitrate, and glycerol act by diminishing the reaction-velocity, whilst lithium chloride and dextrose act by combining with the ferment. It may be noted, in parenthesis, that Van Slyke and Zacharias, in the paper already quoted, give theoretical consideration to a similar distinction between inhibitors. They suggest modifications in their fundamental equation which take account of each type respectively.

Returning once more to the work of Michaelis, a paper with H. Pechstein on the pytalin of saliva[20] must be mentioned in illustration of another side of the subject. It is well known that the diastatic effect of saliva and pancreatic juice is not exerted in the absence of electrolytes. The effect of salts on the activity of the former was first studied on modern lines by S. W. Cole,[21] who attributed the accelerative effects to the anions. It is greatest, he thought, in the case of the salts of strong acids and least in those of weak acids. Michaelis and Pechstein now come to the conclusion that the diastase forms definite complexes with the anions, and it is these complexes, and these alone, that exert the disastatic action. The affinity of the ferment for the anion varies, being very great, for example, for NO_3', not much less for Cl' and Br', and very small for SO_4', and acetate and phosphate ions. The relative activity of the different compounds varies greatly, the chloride being the most powerful, and the nitrate much less so, whilst very much less active are the sulphate, acetate, and phosphate compounds. The optimum hydrion-concentration is different and characteristic for each salt complex. It would appear that other interpretations of the experimental facts dealt with by Michaelis are possible.

Many interesting papers dealing with the special properties of individual ferments must perforce be left without reference. I will close this section by calling attention to a case of catalysis by organic agents which has an interest of its own, although it takes us away from the region of exact studies such as those with which I have been dealing. Several years ago the researches of the Pavlov school brought to light the fact that the proteolytic ferment of the pancreatic juice is secreted in the form of an inactive precursor, trypsinogen, and that this is converted into active trypsin by a catalyst contained in the intestinal juice, and known as enterokinase. The velocity of this activation has been studied recently by H. M. Vernon,[22] and also by J. Mellanby and V. J. Woolley.[23] In each of these researches the fact came to light that the velocity of the process undergoes a positive acceleration, and, towards the end of its course, is enormously increased. Thus, in one experiment, Mellanby and Woolley found that whilst 125 units of active trypsin were produced in the first ninety minutes, after an additional twenty minutes the solution contained 750 units. Vernon,[24] in his latest paper, states that the rate of acceleration during the last half of the process may be a thousand times more rapid than the initial rate. The phenomenon suggests autocatalysis, and Vernon at one time believed that trypsin, once liberated by enterokinase, is itself capable of activating trypsinogen, so that a species of autocatalysis becomes established. Mellanby and Woolley, however, bring evidence against this view, and, moreover, the velocity-curves obtained do not show the **S**-shaped form of ordinary autocatalysis-curves, but indicate rather a continued acceleration of the reaction right up to the point of its completion. Vernon's latest research leads him to the conclusion that "the trypsin liberated in the earlier stages of the reaction by the direct action of enterokinase gradually sets free an enzyme (called *deuterase*, to indicate that it acts secondarily to enterokinase) from a precursor, and that the deuterase is mainly responsible for the later stages of the activation process." The temperature-coefficient of the deuterase-effect is lower than that of the enterokinase-effect, and the later stages of trypsin-activation have a lower coefficient than the earlier. Deuterase, once formed, exhibits linear or logarithmic relations, like other ferments, but the rate of its own liberation as it occurs in mixed pancreatic and intestinal secretions increases in geometrical progression. If no simpler explanation for the facts is forthcoming, this is certainly a remarkable case of physiological catalysis.

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[19] *Biochem. Zeitsch.*, 1914, **60**, 62, 795; *A.*, i, 444, 445.

[20] *Ibid.*, 1914, **59**, 77; *A.*, i, 340.

[21] *J. Physiol.*, 1903, **30**, 202; *A.*, 1904, i, 131.

The Specificity of Tissue-enzymes.

We have long, of course, had to recognise that chemical differentiation underlies morphological differentiation; that the blood- and tissue-proteins of one animal are, for instance, chemically different from those of another; and that within the same animal the proteins of any one tissue are no less distinct from those of any other. Observations made during the last year or two indicate that an equal specificity appertains to the proteolytic enzymes of individual living tissues.

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[22] *J. Physiol.*, 1913, **47**, 325; *A.*, i, 214.
[23] *Ibid.*, 1912, **45**, 370; *A.*, 1913, i, 113.
[24] *Biochem. J.*, 1914, **8**, 494; *A.*, i, 1205.

E. Abderhalden began, so far back as 1906,[25] to test this question by submitting various synthetic polypeptides to the action of organic extracts, and in succeeding years he published many papers showing that there were marked differences to be observed in the peptolytic powers of the various tissues—differences related to the structure and configuration of the polypeptides submitted to their action. Recently he has demonstrated the still more significant fact that the enzymes of a given tissue, whilst they can always hydrolyse peptones made from the proteins of the same tissue, may fail altogether to act on peptones made from the proteins of other tissues. The point is not altogether new. It was foreshadowed in some of the earliest work on autolysis; but Abderhalden has shown that, by testing the action of the enzymes on peptones made from the native proteins rather than on the latter themselves, the facts become technically more easy to demonstrate. Observations on these lines begun by him last year[26] have now been extended, and in conjunction with G. Ewald, Ishiguro, and R. Watanabe[27] he has published experiments showing, for example, that extracts from the liver decompose peptones prepared from that organ, but not those prepared by similar processes from lungs, brain, kidney, or pancreas. A lung extract hydrolyses lung peptones, but not preparations from muscle, liver, or kidney. All observations seem to show that for some reason the renal enzymes have a more general action. One must admit that the technique used to demonstrate these facts is evidently exceedingly difficult, and a repetition of the observations will not be lightly undertaken by others. If, however, relying upon the reputation and experience of Abderhalden, we accept them, they are certainly important and suggestive. The appearance of a highly specific enzyme in the cell, where alone the related and highly specific substrate is to be found, and its appearance in that cell only, are facts which bear, it seems to me, with some significance upon the nature and origin of the enzyme itself. It is important in connexion with what follows to recognise that, according to Abderhalden, the blood does not normally contain ferments which can act on tissue proteins. L. Pincussohn,[28] it is true, in a paper published a year ago, claimed to have found in normal dogs' blood a ferment capable of acting on peptone prepared from dogs' muscle, although it had no action on similar peptones prepared in the same way from cats' muscle, or on other peptones from foreign substances. Abderhalden and G. Ewald,[29] however, could not, in repeated experiments, obtain from normal blood any ferment capable of splitting tissue-peptones, and they claim to have had the remarkable experience of finding that whenever the blood contained a ferment active with the proteins of some particular organ, such activity being observed seventeen times in the course of 1000 examinations, an unsuspected lesion of that organ always proved to be present. The discovery of such ferments in the blood becomes, therefore, of diagnostic importance. This leads to the discussion of related phenomena.

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[25] *Zeitsch. physiol. Chem.*, 1906, **47**, 466; *A.*, 1906, ii, 464.

[26] *Ibid.*, 1913, **87**, 220; *A.*, 1913, i, 1118.

[27] *Ibid.*, 1914, **91**, 96; *A.*, i, 900.

[28] *Biochem. Zeitsch.*, 1913, **51**, 107; *A.*, 1913, i, 788.

Defensive Ferments.

We are still concerned with the work of the indefatigable investigator Abderhalden. His claim to the discovery that the entry of a foreign protein, of a disaccharide, or of a foreign fat, into the circulation of an animal promptly leads to the appearance in the blood of a specific ferment, not there before, capable of hydrolysing the foreign substance, has, chiefly perhaps because of a particular case with practical bearings, to which I shall refer immediately, led to no small excitement in clinical laboratories everywhere. Abderhalden quickly put the results of his earlier experiments, together with his views about their significance, into a book. The first edition of this appeared in 1912, so that the subject is not exactly a new one, but it has hitherto received no notice in these Reports. Its importance, real or supposed, calls for some reference. The current year has seen the appearance of a fourth edition of the book,[30] as well as many fresh papers dealing with the subject.

When proteins are injected into the vein of an animal, reaching the circulation parentally and escaping the digestive mechanism, the blood itself rapidly develops a proteolytic power which it did not possess before. The specificity of the enzyme or enzymes thus called forth, however, is not marked; the circulation of any foreign protein causes the development of a more or less general proteolytic activity in the blood. Very different is the case (according to Abderhalden) when the protein enters in special circumstances.

The pregnant woman carries within her in the form, not of the fœtus, but of the placenta, a source of proteins which are foreign to her own body. As soon as the placenta has formed, its proteins enter the blood-stream, and the formation of a highly specific "defensive" enzyme is the response. The blood of the pregnant woman, and her blood alone, can digest placenta-proteins. No other form of tumour and no pathological conditions of any kind lead to the production of this specific ferment. This is the particular instance of a defensive ferment to which I referred as having caused a flutter in the clinical world. After the phenomenon had been described, Abderhalden's laboratory became crowded with *ad hoc* medical inquirers, all anxious to learn an easy method of getting early information about the coming generation. Why the specificity of the ferment produced should be so much greater than when foreign proteins are injected is not quite clear. Artificial protein preparations seldom, of course, represent pure individual substances, and the method of injection is more brutal and sudden, and likely, therefore, to produce some more general response than when, as in the case of the placenta-proteins, material gradually enters the blood. I have not space to deal fully with the technique of this work. Probably, as this reference to it is somewhat belated, it is already more or less familiar to most. Delicate methods of detecting the digestion of the proteins are required. Either an optical method is used, or the protein (for example, placenta-peptone) is placed, together with a sample of the blood serum, in a small dialyser.

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[29] *Zeitsch. physiol. Chem.*, 1914, **91**, 86; *A.*, i, 896.

[30] "Abwehrfermente der tierischen Organismus," 4th Auflage, 1914.

If digestion occurs, and only then, amino-acids are to be detected in the dialysate. For this detection, the very delicate colour reaction with Ruhemann's triketohydrindene hydrate[31] is used, this substance having been put on the market under the suggestive name of "ninhydrin."

Even more interesting, from some points of view at least, than the response to foreign proteins, is the circumstance that the simpler molecules of a disaccharide can call forth a similar defensive enzyme. Our knowledge as to this fact is really by no means new, for, in 1905, E. Weinland[32] showed that whilst the blood of young dogs is free from invertase, the enzyme appears in it as the result of injections of sucrose. The significance of this observation was not, perhaps, sufficiently appreciated at the time. Five years later similar observations were made in Abderhalden's laboratory with respect to sucrose and lactose. T. Kumagai[33] has published a long paper on the subject in which, in addition to confirming the earlier work, he makes the statement that injection of the monosaccharides lævulose and galactose can call forth invertase. This, Abderhalden and E. Bassani[34] are unable to confirm. With regard to the influence of sucrose, it seems that, on the whole, the response can be got with more certainty from rabbits than from dogs.[35] Kumagai, in the paper mentioned, claimed that an independent and altogether remarkable property is acquired by the blood-serum as a result of the injection of sucrose. It is said then to act on dextrose and lævulose, first converting the former into the latter, which next suffers synthesis into a disaccharide. The observations were made in F. Röhmann's laboratory at Breslau. A later paper published by Röhmann and Kumagai[36] conjointly, contains the supposed proof that the disaccharide is lactose. That the injection of sucrose should call into the blood a catalyst capable of converting, outside the body, dextrose into lactose is a truly extraordinary event. The evidence as described is conclusive enough, but one cannot but feel scepticism, and it is to be hoped that the experiments will be repeated. If the facts are as stated, they are of great physiological importance.

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[31] *T.*, 1910, **97**, 2025.

[32] *Zeitsch. Biol.*, 1905, **47**, 279; *A.*, 1905, ii, 730.

[33] *Biochem. Zeitsch.*, 1914, **57**, 380; *A.*, i, 112.

[34] *Zeitsch. physiol. Chem.*, 1914, **90**, 369; *A.*, i, 765.

It seems to be, at any rate, of quite exceptional interest to know that an immunity reaction as represented by the production *de novo* of a more or less specific hydrolytic ferment may be called out by simple molecules such as those of the disaccharides. In connexion with the immunity-phenomena of disease we are too much accustomed to think of the colloid nature of toxins as playing some essential part.

How precisely the ferments under discussion are to be related to the factors of immunity as recognised in other connexions is not yet clear. A. Hauptmann[37] and others suggest that the defensive ferments, like other anti-substances, are probably constructed on amboceptor-complement lines, the complement representing, as usual, their unspecific, and the amboceptor their specific, constituent. Abderhalden protests against the intrusion of Ehrlich's complex nomenclature into the description of phenomena that are probably simpler than those to which it was intended to apply. We may recall here, however, the Armstrongs' views as to the nature of ferments in general (see above), and, in any case, the hydrolytic action of the defensive ferments and the phenomenon seen, for instance, in hæmolysis are probably related. That the action of the defensive ferments is in some way related to anaphylaxis[38] is nearly certain.

Many papers on the defensive ferments published during the year in the technical medical journals have been of a critical sort,[39] especially in connexion with the placenta-reaction, which does not seem to be successful in the hands of all. A. G. Hogan,[40] moreover, could find no improved utilisation of sucrose or lactose as the result of repeated intraperitoneal injections of these sugars. He did not study the action of the serum, but holds that his results prove that no "immunity" was developed, and that the physiological significance of Abderhalden's results is therefore doubtful. We may have to wait some time before the whole subject can be viewed in proper perspective.

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[35] Abderhalden and F. Wildermuth, *Zeitsch. physiol. Chem.*, 1914, **90**, 385; *A.*, i, 765; Abderhalden and L. Grigorescu, *ibid.*, 419; *A.*, i, 765.

[36] *Biochem. Zeitsch.*, 1914, **62**, 1; *A.*, i, 766.

[37] *Münch. med. Wochensch.*, 1914, 1167.

[38] *Ann. Report*, 1910, 201.

[39] Compare L. Flatow, *Münch. med. Wochensch.*, 1914, 1168.

Some Aspects of Intermediary Metabolism.

Carbohydrates and Fats.—The fate of sugar in the body remains a prominent subject of research. Its secrets are strongly entrenched, but an army of investigators is "nibbling" at them and not without success, although the moment for a decisive advance seems not yet to have arrived. I gave a good deal of space to the subject last year, and must be somewhat briefer here.

The growing conviction that one aspect at least of the metabolism of sugar involves a preliminary non-oxidative cleavage resulting in the production of lactic acid is, in a sense, greatly strengthened by the researches of J. Parnas and R. Wagner[41] on amphibian muscle. That the lactic acid of muscle takes origin from its carbohydrates has, of course, been long suspected, but I know of no other experimental work that makes the relation between them so clear. The origin of one from the other is probably not indeed, in the strictest sense, direct, but Parnas and Wagner make it nearly certain that the lactic acid arises from a precursor which stands in intimate genetic relation to the carbohydrate.

Evidence pointing, although I think with considerable less cogency, in the same direction is advanced by O. von Fürth.[42]. Only if the diet of rabbits be rich in sugar is there, in these animals, any excretion of lactic acid as the result of phosphorus poisoning. In the absence of carbohydrates there is none. As the increase is, in any case, relatively small, the author suggests that his experiments indicate that the origin of lactic acid from sugar is through some intermediary substance, and not direct. There is indeed good reason to believe that in the muscle fibre the carbohydrate is synthesised into some complex, and from this the lactic acid more directly arises. There is little doubt, however, that sugar suffers also a more direct degradation in the body.

In the endeavour to discover what compounds are related to sugar in the processes of metabolism, many workers have continued to use

[40] *J. Biol. Chem.*, 1914, **18**, 485; *A.*, i, 1157.

[41] *Biochem. Zeitsch.*, 1914, **61**, 387; *A.*, i, 772.

[42] *Ibid.*, 1914, **64**, 131; *A.*, i, 1014.

Lusk's method, which is based on quantitative studies of phloridzin diabetes. It is clear that any information regarding the nature of the substances that can yield sugar in the diabetic animal bears also on the fate of sugar itself in the normal animal. It is changes in chemical equilibrium in one direction or the other that occur.

In Lusk's method a dog is given phloridzin under carefully standardised conditions, and its output of sugar and nitrogen determined. If the addition to a uniform dietary of the substance under study results in an increase of urinary sugar, without disturbance in the output of nitrogen, it is assumed that the substance is directly converted into sugar. If it acts only indirectly, increasing sugar by increasing metabolism, then the nitrogen will be increased also. In the former case the amount of "extra" sugar formed will be some guide as to the chemical processes involved. It may indicate, for instance, whether all, or only some, of the carbon atoms present in the molecule of the substance being studied are concerned in the formation of sugar.

Lusk's method seems usually to give trustworthy and definite information, and the more one learns about the truly remarkable action of phloridzin in determining that everything capable of yielding sugar in the animal body shall be promptly excreted as sugar, the more does one desire better information concerning the precise mechanism of its action. The extensive use in recent years of the drug has helped us but little in this respect. To A. I. Ringer and E. M. Frankel[43] we owe some information as to the time relations of the glucogenetic phenomena. They find that after the administration of dextrose itself the curve of sugar-elimination reaches in two hours a point which, after the administration of such a precursor as propionic acid, is only reached in four or five hours. There is a definite time required for the processes of conversion.

With regard to the nature of substances capable of yielding sugar I will refer only to the papers of the present year. Ringer and Frankel[44] find that dihydroxyacetone is glucogenetic, and, in one experiment at least, it was quantitatively converted into dextrose in the phloridzinised dog. I. Greenwald[45] states that the same is true for citric acid, and F. Schwenken[46] claims to have obtained sugar quantitatively from acrylic acid. The work of the last few years has shown that, whilst some substances which we might expect to yield sugar easily wholly fail to do so, positive results are obtained with a number of substances of very diverse

[43] *J. Biol. Chem.*, 1914, **18**, 81 ; *A.*, i, 902.

[44] *Ibid.*, 233 ; *A.* i, 1025.

[45] *Ibid.*, **17**, xxxiv ; *A.*, i, 629.

[46] *Beitr. Physiol.*, 1914, **1**, 140 ; *A.*, i, 1156.

constitution, a noteworthy proportion of these being compounds with three carbon atoms in the molecule. Every result obtained with this technique is of value as illustrating chemical possibilities in metabolism, but it is sure that some caution may be necessary before it is concluded that every substance proved on these lines to be glucogenetic is really an intermediary in the normal metabolism of carbohydrates.

Sometimes the phloridzin method gives uncertain results. I mentioned last year that whilst the claims of pyruvaldehyde (methylglyoxal) to be a normal intermediary metabolite have much to support them, those of pyruvic acid are less clear. A. I. Ringer, who has had much experience of the method, states that pyruvic acid when administered to the phloridzinised animal sometimes gives large quantities of dextrose and sometimes none at all. Either the condition of the animal becomes an important factor, or else idiosyncracy enters into the phenomenon. The results suggest, to my mind, that the acid is a foreign substance, and not a normal obligatory stage in sugar metabolism. P. A. Levene and G. M. Meyer[47] confirm this view, for they find that isolated animal tissues which, as we know, rapidly act on pyruvaldehyde, have, under aseptic conditions, no effect on the acid. I must not forget indeed that I. Smedley (Mrs. MacLean) and Eva Lubrzynska[48] have advanced an ingenious hypothesis suggesting that pyruvic acid, formed in the body as a decomposition product of carbohydrate, is the starting point for the physiological synthesis of fatty acids. Better evidence for the physiological nature of pyruvic acid seems called for, however. Ringer and Frankel,[49] in an endeavour to analyse the precise fate of this acid when administered, have observed an interesting set of facts with somewhat special bearings. When acetaldehyde or propaldehyde is injected into a phloridzinised animal there is a large absolute increase in the dextrose eliminated, greater indeed than would occur if the whole of the aldehyde were converted into sugar. This is associated not with an increase, but with a decrease in the loss of nitrogen to the body, and there is also a marked decrease in the excretion of acetone, β-hydroxybutyric acid, and acetoacetic acid. Clearly something more complicated than direct conversion occurs. The effect of the aldehyde is remarkable, since neither ethyl alcohol nor acetic acid has any appreciable influence on the metabolism of the diabetic dog, whilst propyl alcohol and propionic acid, although known to suffer direct conversion into sugar, do not produce the

[47] *J. Biol. Chem.*, 1914, **18**, 469; *A.*, i, 1157.

[48] *Biochem. J.*, 1913, **7**, 364; *A.*, 1913, i, 1014.

[49] *J. Biol. Chem.*, 1914, **16**, 563; *A.*, i, 357.

secondary effects mentioned. It would seem as though the aldehyde group must exercise a special influence. The facts indeed have led Ringer to consider the possibility that dextrose itself may owe its power of inhibiting the excretion of the acetone substances (its "antiketogenetic" action) to its aldehyde group. In special experiments he found that gluconic acid, although differing from dextrose only in the replacement of the aldehyde group by carboxyl, has no antiketogenetic power. He advances finally a theory of diabetes and of acidosis on lines somewhat similar to those foreshadowed in my Report last year. When β-hydroxybutyric acid arises from the oxidation of fatty acids and amino-acids in metabolism, it forms, under normal conditions, a glucoside with dextrose, and only in this combination is it further metabolised. In diabetes (experimental or clinical) the power to form this glucoside union is absent, and its failure is at the bottom of all the chemical disturbances. Such, very partly and incompletely stated, is Ringer's thesis, and in the paper quoted he supports it with ingenious arguments.

W. M. Marriott,[50] however, calls attention to the fact that the diabetic, whilst unable to deal with *l*-β-hydroxybutyric acid, fully oxidises the corresponding *d*-acid. To explain this on Ringer's lines, he ventures upon the hypothesis that the *d*-acid combines with the β-form of dextrose, whilst the *l*-acid requires the α-form, in which the diabetic is presumably deficient. By this time, however, the theory has got far beyond the facts.

We are still far from being able to describe fully the events of carbohydrate metabolism, but it is sure that ultimate success will arise from experiments based on clear thought on chemical lines. The influence of the nervous system and the balance of glandular activities condition events in the body, but the ultimate events themselves are chemical. They are definite molecular reactions proceeding smoothly in health whilst interrupted and diverted in disease.

It is sure, of course, that apart from the effect of disturbances in the internal secretions of the body the normal progress of these reactions, like that of other chemical events in the body, is affected by less specific factors, as by variation in the hydrion-concentration in the blood and tissues. P. Rona and G. G. Wilenko have shown, in two interesting papers, how marked is the influence of this factor on the utilisation of sugar by the heart,[51] and on the glycolysis[52] which occurs in the blood.

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[50] *J. Biol. Chem.*, 1914, **18**, 241.

[51] *Biochem. Zeitsch.*, 1914, **59**, 173 ; *A.*, i, 350.

[52] *Ibid.*, 1914, **62**, 1 ; *A.*, i, 766.

An excised heart kept active by artificial perfusion is an admirable object for the study of such factors quantitatively, and the authors quoted show that extremely small departures from a normal hydrion-concentration, in the direction of acidity, in the fluid perfused prevents the consumption of sugar by the surviving organ. Similar small departures from a normal reaction inhibit the familiar disappearance of sugar which occurs when normal blood is kept. It is clear that these facts are of much importance in connexion with the acidosis which is characteristic of diabetes. I have discussed in considerable detail the effects of changes in the reaction of the body fluids on physiological processes in the Oliver-Sharpey lectures for the current year (*Lancet*, 1914).

The Creatine Problem.—This elusive but always attractive subject has been well to the front during the year. What is the meaning of the creatine of muscle; what is its origin; and what its relation to urinary creatine and creatinine? A truly astonishing amount of good and quantitative work has been put into the endeavour to find answers to these questions; but the answers are not yet complete. O. Folin, to whose methods we owe the possibility of quantitative study, has himself returned to the ground this year. Before reviewing what he has written, however, I will deal with a paper by S. R. Benedict and E. Österberg,[53] because a reference to their work and views follows logically, as will be seen, on my discussion of the phenomena due to phloridzin injection. Creatine is known to appear in the urine of adults as the result either (i) of starvation, inanition, and general conditions involving loss of body tissue, or (ii) of failure on the part of the body to obtain or make due use of carbohydrate, as in diabetes. Either of these may be looked upon as the essential cause of creatinuria, and be considered as involving the other. Some believe that the origin of the urinary creatine is to be sought alone in tissue-wastage, which involves an abnormal liberation of tissue (muscle)-creatine. From this point of view it is easy to indicate that excessive tissue-waste is characteristic of diabetes, and the undoubted experimental fact that giving carbohydrate alone, without protein, will prevent the excretion of creatine during inanition, can be explained as merely a part of the ordinary sparing effect of carbohydrate on protein metabolism. It spares the muscle protein structure and therefore prevents the liberation of the associated creatine. On the other hand, there are those who believe, following a suggestion originally due to Cathcart, that creatine is a substance the functions and fate of which are intimately bound up with the normal processes of carbohydrate metabolism. When the latter are in abeyance, as in diabetes, the creatine, which is otherwise used, perhaps synthetically, in metabolism, appears in the urine. From this point of view the effect of general starvation in inducing creatinuria is actually the result of specific carbohydrate starvation, and the preventive effect of giving carbohydrate alone has been held to prove it. To these two alternatives Benedict and Österberg addressed themselves. They realised that the phloridzinised animal, which suffers both from an increased nitrogenous breakdown and from inability to use carbohydrate, is an excellent experimental object on which to test them. They worked, therefore, with animals under the influence of this drug and under various nutritive conditions. The dogs, when fasting, lost flesh rapidly, and their excretion of creatine was high. Benedict and Österberg's experiments, however, at once established the crucial fact that if the animals were fed with creatine-free protein food, in such amounts that the loss of nitrogen to the body was covered and even more than covered, the high elimination of creatine remained quite unaffected. The figures obtained served "to demonstrate beyond any argument that the creatine eliminated by these phloridzinised animals did not represent creatine preformed in the muscle, and that muscle 'disintegration' played no part in furnishing the creatine put out." Now when the animals at the close of the experiment were killed, it was found that the total creatine of the muscle, in spite of the prolonged hyper-excretion of the substance, was by no means reduced, but was in excess of the normal. This the observers held to be due to the circumstance that, because utilisation of creatine is prevented by the drug, a large amount circulates, and the tissues become more than normally saturated with it. The fact is in any case not in harmony with the view which has been held by some that the total creatine of the muscles is depleted in proportion to the amount eliminated in the urine. The experiments indicate, indeed, that creatine is normally produced, and subsequently used or destroyed, in larger amounts than is usually supposed. In simple fasting the amount excreted daily is but small, but this yields no evidence as to the amount actually produced, any more than a minimal grade of glycosuria, resulting in the excretion of a few grams of sugar in the day, would be a measure of sugar-production in the body. Phloridzin makes the animal "diabetic" in respect of creatine, as well as in respect of sugar, and the drug, by interference with their normal utilisation or destruction, brings them both to light in the urine. Benedict and Österberg conclude that the fate of the one substance is related to that of the other, and are themselves in agreement with the view that the power of the organism to metabolise the creatine which it forms "is directly related to certain processes chief among which appears to be the utilisation of carbohydrate."

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[53] *J. Biol. Chem.*, 1914, **18**, 195; *A.*, i, 1025.

O. Folin has published papers during the year dealing with the technical side of the subject, and has given us important improvements in the methods for estimating creatine and creatinine in the urine, blood, and tissues, as well as supplying experimental data relating to the creatine in each of these. To judge, however, from a paper published conjointly with W. Denis,[54] his mind has been occupied with an aspect of the subject which, if fundamental, is somewhat special. He is concerned for the moment, not so much with the dynamics of creatine, but with the question as to what precisely is the nature of its association with muscle substance. "Creatine must," write Folin and Denis, "be a waste product or a synthetic product serving some special function, or as a synthetic product it may in fact be a part of the living active protoplasm. We believe that the last-named alternative represents the facts, and in support of this hypothesis we now propose to show that the so-called creatine of muscle is a post-mortem product, and there is very little creatine in living muscle."

The last statement implies that, when our estimations of creatine are made, the mechanical destruction of the muscle fibres liberates the base from a complex in which its identity had been in some sense or other submerged. It is not clear, to me at least, when creatine (or any other tangible tissue constituent) is spoken of as being "part of the living active protoplasm," whether it is supposed to exist in some large molecule, from any part of which the creatine structure is wholly absent, but whence the base emerges with its own identity established as the result of extensive molecular rearrangements at the moment of protoplasmic death, or whether creatine *qua* creatine is supposed to be linked up in a complex and merely liberated post-mortem by such a process as hydrolysis. Folin and Denis seem clear at any rate that the living muscle does not contain free creatine, nor, as I understand them, any loose adsorption compound of the base. Their proof of this is, however, by no means a direct one. They argue somewhat as follows. Muscle yields, post-mortem, from forty to fifty times as much creatine per 100 grams of substance as ever blood is found to contain. It cannot, therefore, be in ordinary equilibrium with the blood. There is evidently "some definite effective force or condition by which the creatine is held fast in the muscle." When fresh creatine enters the blood it is freely taken up by the already creatine-laden tissues, a fact for which new experiments described in the paper now being quoted give further evidence. If I understand the authors rightly, it is essentially this disproportion between the concentration in the blood and muscle which has led them to their very wide-reaching conclusion. Without asserting that the creatine in muscle is simply adsorbed, I feel wholly unable to admit that the disproportion as discussed cannot be explained by the formation of an ordinary adsorption compound with the muscle colloids. In one of the experiments given in the paper an anæsthetised dog, the muscles of which had yielded on preliminary analysis 544 mg. of creatine per 100 grams of tissue, received 3 grams of the base by way of the small intestine. As a result the muscles yielded, after a certain interval, 689 mg. per 100 grams, showing an increase of 26 per cent. Now the extra 145 mg. could hardly have come to form part of the bioplasm during the course of the experiment. Few at least of those who conceive of the bioplasm as an entity, distinct from the general metaplasmic cell contents, would admit that, as the result of a mere increase in the supply of a given constituent, it could immediately suffer so considerable a change in its constitution. If it could undergo any such constitutional changes as the result of variations in supply, the recognised distinction between exogenous and endogenous metabolism would hardly be justified. On the other hand, if it be supposed that the extra amount of creatine found had not yet had time to be assimilated, the data of the experiment show that the muscle with 145 mg. of free creatine per 100 grams was in equilibrium with blood containing only 80 mg. If this difference can exist without the hypothetical entry of the base into the muscle protoplasm there is no good reason to believe that larger differences could not exist on similar terms.

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[54] *J. Biol. Chem.*, 1914, **17**, 493; *A.*, i, 767.

I do not pretend to know as much about the physiology of creatine as does Folin, and I owe to him most of what I do know about it, but I have ventured on this discussion because I feel that certain conceptions which underlie the argument used by Folin and Denis in their paper have a general bearing on our views respecting equilibrium in the living cell, and are, in my opinion, likely to confuse the issues.

Many other papers which have dealt with creatine and creatinine during the year cannot be quoted here. The physiological independence of the two substances originally demonstrated by Folin seems to be fully illustrated by the work of Benedict and Östeberg, although Schaffer seems inclined to support Morris and Fine in returning to the older view that the latter arises within the muscle from the former as a precursor. Folin himself now teaches that "when a tissue dies the post-mortem product, creatine, is set free, whereas in the course of the normal replaceable breakdown, which we call tissue-metabolism, the product split off is usually (normally) not creatine but creatinine." Whether on these lines they have a common precursor of a more definite sort than the bioplasm itself he does not say. It would certainly be remarkable if two metabolites so intimately related chemically should have no relation at all in metabolism.

The extraordinary steadiness of creatinine-output during very wide fluctuations in exogenous nitrogen which has led us, again under Folin's guidance, to regard its amount as the best measure of essential tissue-metabolism, is once more strikingly confirmed in a paper by A. E. Taylor and W. C. Rose.[55] When, by altering the protein intake, the urinary nitrogen was made to vary between 7·4 grams and 30·2 grams, the creatinine only varied between 0·63 and 0·68 gram.

Vitamines.

Interest continues to be centred in those accessory food substances of unknown nature for which Funk proposed the now familiar name of vitamines.

T. B. Osborne, L. B. Mendel, and Edna L. Ferry[56] find that the substances in milk which have a specific effect in promoting growth in young animals can be separated with the butter-fat. Their solubility in fats is further illustrated by the work of E. V. McCollum and Marguerite Davis,[57] who find that if fresh butter is saponified and the aqueous solution of its soaps extracted with olive oil dissolved in ether, the oil left on evaporation of the ether has acquired the property of promoting growth. This observation, unfortunately, does not help us in an endeavour to isolate the vitamines. It is uncertain as yet whether the substance necessary for growth is the same as that which can cure the neuritis which develops in fowls fed on polished rice, and the absence of which from a diet is supposed to be responsible for the disease beri-beri. Funk[58] found that polished rice and a vitamine-containing fraction from yeast constitute together a complete food, and decided that, as the yeast preparation used in these experiments contained no phosphorus, the importance of the phosphorised lipoids in "deficiency diseases" is probably small. With A. B. Macallum[59] he has published observations which do not altogether agree with

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[55] *J. Biol. Chem.*, 1914, **18**, 519; *A.*, i, 1151.

[56] *Ibid.*, 1913, **16**, 423; *A.*, i, 107.

[57] *Ibid.*, 1914, **17**, 245; *A.*, i, 1188.

[58] *J. Physiol.*, 1914, **48**, 228; *A.*, i, 768.

[59] *Zeitsch. physiol. Chem.*, 1914, **92**, 13; *A.*, i, 1017.

Osborne and Mendel's statements as to the vitamine content of butter. It was found, further, that cod-liver oil added to polished rice prevents neuritis from developing, but does not promote growth, so here at least we seem to have evidence for the existence of more than cne type of vitamine. This paper contains a photograph showing an extraordinary difference in the development of chickens fed with and without the necessary vitamine supply.

E. A. Cooper[60] has continued some investigations on the amount of anti-neuritic substance in certain practical food-stuffs. The chief point that arises from his researches is that voluntary muscle is poor in the vitamine, so that meat should be supplemented by other foods in the treatment of beri-beri. A hitherto unsuspected effect of the absence of these accessory substances from the diet is suggested in a preliminary way by experiments made by Funk and Count E. von Schönborn.[61] They find that pigeons fed on artificial food mixtures develop an abnormality in metabolism leading to a marked hyperglycæmia and a diminution of glycogen in the liver. This condition was apparently cured by giving a vitamine fraction from yeast.

No one could be more assured than I am (after a good many years of experiment) of the real existence and of the nutritive importance of these accessory food substances, but I am equally sure that as yet we know nothing of their chemical nature. J. C. Drummond and C. Funk[62] have just published a paper which is significant in its admissions. In my opinion we have now no trustworthy evidence for the activity as vitamines of any of the crystalline substances which Funk has from time to time separated and described. The paper last mentioned deals with the complete fractionation of a crude vitamine fraction from rice polishings. From the polishings Funk[63] some time ago separated and described a substance, $C_{26}H_{20}O_9N_4$, melting at 233°, together with nicotinic acid. The former supposititious substance, however, is now admitted, as the result of further study, to be also nicotinic acid, and this is not a curative material at all. No crystalline substance with power to cure neuritis has really been separated from rice polishings.

From yeast, on the other hand, Funk once obtained a "curative" substance to which the formula $C_{24}H_{19}O_9N_5$ was ascribed. The melting point of this was 225°, but a substance prepared earlier from the same source by similar methods melted at 233°, and the two were identical in crystalline structure, solubility, and reactions.

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[60] *J. Hygiene*, 1914, **14**, 12 ; *A.*, i, 777.

[61] *J. Physiol.*, 1914, **48**, 328 ; *A.*, i, 1015.

[62] *Biochem. J.*, 1914, **8**, 598.

[63] *J. Physiol.*, 1913, **46**, 173 ; *A.*, 1913, i, 936.

Now of this last substance, when first described, it was remarked: "Recrystallised from dilute alcohol the substance melts at 233°, at the same temperature as the curative substance from rice. It gives the same reactions, and both substances must be therefore considered as identical."[64] The substance from rice, melting at that temperature, is, however, as we now learn, nicotinic acid, and it is difficult to avoid the suspicion that the first-mentioned yeast product, in spite of the elementary analysis (done by Pregl's method on 3 to 4 mg. of substance), was nicotinic acid also. In any case the yeast product showed appreciable curative effects only when mixed with what was avowedly a nicotinic acid fraction from the same source, and the latter (although pure nicotinic acid is without action) had itself some curative effect. There is not, I think, a great deal to be said for the substance, $C_{24}H_{19}O_9N_5$, as a crystalline vitamine. As Drummond and Funk were quite unable to confirm the work of Suzuki, Shimamura, and Odake,[65] who claimed to have separated the active substance from rice in the form of a picrate, we have evidently no certain knowledge of any pure substance with the properties of a vitamine.

F. G. HOPKINS.

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[64] *J. Physiol.*, 1912, **45**, 76.

[65] *Biochem. Zeitsch.*, 1912, **43**, 89; *A.*, 1912, ii, 980.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

Although for the year 1914 no results of exceptional importance have to be recorded, a number of investigations of considerable interest relating to soils and plant nutrition have been carried out. The soil problems which have received most attention are those connected with partial sterilisation, absorption of bases, acidity, and the production and movements of nitrates in soils, whilst in the case of plant nutrition a good deal of attention continues to be given to the question of stimulants.

At the meeting of the International Commission on the Chemical Analysis of Soils, which was held in Munich in April,[1] the subjects discussed included: (1) the preparation of soil extracts for total analysis; (2) the estimation of readily soluble soil constituents; and (3) the estimation of soil acidity.

On the assumption that the double silicates in soils belong to two sharply defined groups, those of the one group readily giving up their bases when treated with a 10 per cent. solution of an electrolyte, whilst those of the other group, representing the unweathered rock, are acted on very slowly, a provisional method has been devised in which the soil is treated with 10 per cent. ammonium nitrate solution. It was found that the main portion of the bases which dissolve at all was contained in the first 50 c.c. of the filtrate.

It was, however, decided, for obtaining a standard method, to confine attention for the present to extraction with water containing carbon dioxide.

Of the publications which have appeared during the year may be mentioned: "Ernährungsphysiologisches Praktikum der höheren Pflanzen," by V. Grafe; "Die Typen der Bodenbildung," by A. Glinka; "Grundzüge der Pflanzenernährungslehre und Düngerlehre," by W. Kleberger; a third edition of Tollens' "Kurzes Lehrbuch der Kohlenhydrate," and a third edition of Wahnschaffe's "Wissenschaftliche Bodenuntersuchung."

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[1] *Nature*, 1914, **93**, 598.

The Atmosphere.

A useful series of analyses of rain-water has been made in South Africa,[2] extending over one or two years in the case of Grahamstown, Kokstad, Bloemfontein, Durban and Cedara, and for shorter periods at several other places. It is shown that at Grahamstown and Kokstad the total nitrogen, as ammonia and nitrates, amounts to only 1·88 and 2·00 kilos. per hectare per annum, which is about half the amount found at Rothamsted. The difference is mainly in the ammonia–nitrogen, which at Grahamstown amounts to only 1·06 kilos., and at Kokstad to 1·25 kilos., per hectare. At the other places much higher results were obtained, the total nitrogen varying from 5·47 to 6·98 kilos. per hectare, owing perhaps, in part, to contamination with dust, etc., especially in the northern parts of the Union, where dust storms are very frequent. The high results are all due to much larger proportions of ammonia, especially at Cedara (5·28 kilos.), where the nitric nitrogen is quite normal (0·97 kilo. per hectare). The analyses include chlorides, and in some cases sulphates as well.

An important investigation of rain collected in towns has been undertaken by the Committee for the Investigation of Atmospheric Pollution,[3] which has already published some monthly results obtained at a number of towns. All the samples are collected in gauges of a standard type, and a standard method is employed for analysing the rain and other deposits, so as to obtain comparable results.

The series of analyses of rain commenced some years ago at Ottawa[4] are being continued, and some analyses of rain and snow have been made during a few months at Mount Vernon, Iowa.[5]

Soils.

Acidity in soils is generally to be attributed to the decomposition of organic matter under unfavourable conditions, or to an excessive employment on non-calcareous soils of salts of which the bases are mainly utilised by plants. Instances have also occurred of acidity brought about by the oxidation of iron sulphide.

Recent experiments in Japan[6] have shown that acidity occurs in certain sandy soils containing only small amounts of humus, and that this mineral acidity is due to aluminium and iron compounds

[2] C. F. Juritz, *South African J. Sci.*, 1914, **10**, 170; *A.*, i, 916.

[3] *Lancet*, 1914, ii, 1010, 1110.

[4] F. T. Shutt, *Exper. Farms Rep.*, 1914, 265.

[5] G. H. Wiesner, *Chem. News*, 1914, **109**, 85; *A.*, i, 472.

[6] G. Daikuhara, *Bull. Imp. Centr. Agric. Exper. Stat. Japan*, 1914, **2**, 1; *A.*, i, 1211.

absorbed by soil colloids. It was found that the application of ammonium sulphate, disodium hydrogen phosphate, and potassium chloride to a granite-sandy soil resulted in a reduction of the small yield of barley, obtained in the unmanured soil, to almost nothing; whilst with a further addition of calcium carbonate the yield was enormously increased. The manured soil was so strongly acid that the zinc pots in which the experiments were made were perforated. Further investigation showed that the majority of Japanese and Corean soils examined were acid, and that in at least half of them the acidity was due, in part, to colloid absorption of aluminium and iron compounds. As regards geological origin, it is shown that soils from Mesozoic formations are the most frequently acid, then Tertiary, Palæozoic, and diluvium soils.

A number of zeolites which were neutral to litmus became acid after treatment with acetic acid, or extraction with a solution of potassium sulphate. Acid kaolins behave towards neutral salt solutions the same as acid soils, and similar results are obtained with alkaline kaolins, after they have been treated with dilute acids; and with granite and other alkaline rocks which have been subjected to the action of aqueous carbon dioxide for some weeks. Similarly, the acidity of the soils is increased by treatment with dilute acids; mineral acids and formic acid were found to have the greatest, and about equal, effects, whilst with acetic acid the increase in acidity was much less, and with oxalic acid very much less.

The filtrates from acid soils which have been treated with a neutral salt solution give with ammonia precipitates consisting chiefly of aluminium hydroxide, the amount of which corresponds with the acidity of the soil and with the amount of *N*-alkali used in the titration, whilst the filtrates from neutral soils and aqueous extracts of acid soils give no precipitate.

The acidity of soils after treatment with different salts varies considerably, according to the salt employed. With chlorides, the highest acidity was obtained with potassium salts; sodium, magnesium, and calcium chlorides produced only about half the acidity or less. Of the different potassium salts, the chloride and the nitrate give the greatest acidity, whilst the chlorate, sulphate, and iodide gave respectively 90, 80, and 76 per cent. of the acidity produced by the chloride, taking the averages of a number of soils. As regards the degree of acidity produced by potassium chloride solutions of different strengths, it was found that the acidity increases rapidly at first, and more slowly afterwards, as the strength increased from $N/50$ to N; in one case the maximum was reached at this point, whilst further slight increases were obtained in other soils with stronger solutions.

From some of the results the conclusion might be drawn that the acidity of mineral soils is due to kaolin or acid silicates. In this case, kaolins should be strongly acid, and should part with a good deal of aluminium when treated with a salt solution. Kaolins are, however, sometimes neutral, and even alkaline, whilst acid kaolins only give up small amounts of aluminium when treated with potassium chloride. Both kaolins and soils, when treated with aluminium and iron chloride solutions, absorb varying amounts of the bases and become acid, or, if acid, more so. Iron absorbed in this manner is displaced by aluminium, but not aluminium by iron; the absorbed aluminium and iron are partly redissolved by potassium chloride solution. It seems probable that when neutral or alkaline soils acquire acid properties by treatment with acids, the aluminium or iron compounds, produced by the action of acid, are absorbed by colloids and their positive ions replaced by the basic ions of the neutral solution.

Some of the results just referred to have been obtained in an independent investigation on adsorption,[7] in which it is also shown that the acidity produced in kaolins and soils by the action of acids is not due to absorption of acid; soils which had been treated with sulphuric acid, washed with water, and extracted with potassium nitrate solution failed to give up any further amount of sulphuric acid. It was also found that soils which were boiled for some time with concentrated sulphuric acid acquired the same degree of acidity, when treated with potassium chloride solution, as another sample which was treated with $N/40$-acid. In another experiment, soils and kaolin were treated with hydrochloric acid and then with barium chloride. They were then washed, again treated with hydrochloric acid, and the barium estimated; the amount recovered corresponded with 95 per cent. of the acid liberated by the soil from the barium chloride, and with 89 per cent. in the case of kaolin.

Another case of soil acidity has been noticed in Assam.[8] The soil is an old alluvium and a light loam in a good physical condition, but deficient in phosphoric acid and especially in calcium carbonate. Although some crops, such as *Phaseolus mungo*, will grow on the soil, most others, such as oats and grain, die as seedlings unless considerable amounts of lime are added. As a result probably of the acid conditions, the soil contains an organic acid which, in the free state, is very toxic to *Andropogon sorghum*, but not to all kinds of plants; it even acts as a stimulant with paddy-rice. The results of a number of plot experiments with and without lime showed that the only unlimed plots that gave any material crops were those which received alkaline manures, and some which had superphosphate. The action of the latter manure in saving the crop, notwithstanding the increased acidity, is attributed to its stimulating action on root growth, which would result in increased oxidation and in the destruction of the toxic substance.

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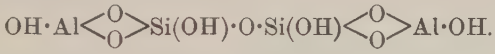
[7] J. E. Harris, *J. Physical Chem.*, 1914, **18**, 355; *A.*, i, 653.

[8] A. A. Meggitt, *Mem. Dept. Agric. India Chem. Ser.*, 1914, **3**, 235; *A.*, i, 1212.

Acid clays and loams also occur in considerable amounts in Porto Rico,[9] where they have an intense red colour, due to the very complete weathering and the breaking down of the iron silicates to iron oxide and silica. The climatic conditions which favour the production of these soils are frequent rains in hot summers, which wash out the bases, and if such conditions prevailed when the clays were being produced from felspars, the bases would be washed away, as soon as liberated, by the co-operation of carbon dioxide. As regards the constitution of the acid clay, the following formula is suggested, as it admits the absorption of phosphoric acid as well as of bases:



$$\mathrm{OH\cdot Al}<\substack{\mathrm{O}\\ \mathrm{O}}>\mathrm{Si(OH)\cdot O\cdot Si(OH)}<\substack{\mathrm{O}\\ \mathrm{O}}>\mathrm{Al\cdot OH}.$$

Although the subject of humus, or of those portions of it which dissolve in water or in alkali, continues to receive a fair amount of attention, no very definite results have been published during the year. The existence of humic acids seems no longer to be disputed; it is now rather a question of the relative importance of humic acids and of colloids which absorb bases, since the presence of both is recognised.

By extracting *Sphagnum* peat with water as long as anything is dissolved, two distinct colloids have been obtained; and a non-colloid, which is supposed to consist mainly of Berzelius' apocrenic acid. After subsequent extraction with $4N$-ammonia until nothing remains but fibres, undecomposed wood, and a black substance, a solution is obtained which contains another acid, perhaps crenic acid.

Suspensions of *Sphagnum* and of *Sphagnum* peat behave very differently when treated with ammonia, the peat yielding large amounts of salts, whilst the *Sphagnum* itself does not, and it is shown that the effect on conductivity of the production of salts from the peat exceeds that of adsorption even in concentrations of $0{\cdot}01N$. No decomposition can very well occur, since humates are extracted even by $0{\cdot}005N$-ammonia solutions.

The hard, brittle, insoluble modification of humic acid obtained by heating at 100° can be rendered soluble by prolonged treatment with alkali, and the transformation can be followed by means of conductivity measurements.[10]

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[9] O. Loew, *Landw. Jahrb.*, 1914, **46**, 161.

It has been shown[11] that acid peats sometimes yield as much soluble humus when directly treated with alkali as when previously extracted with acid, and that even some alkaline peats give up more than half the total soluble humus when directly treated with alkali.

Alkaline peats, when hydrolysed with 20 per cent. hydrochloric acid, yielded small amounts of ammonia, whilst in the case of acid peat no ammonia was formed.

When solutions containing equivalent amounts of ammonium and potassium hydroxides are employed for extracting humus, it is found that ammonia extracts the larger amount of nitrogen.

In an investigation of some Hawaiian soils,[12] it was found that the amount of ammonia present was usually considerably in excess of the nitrates. The amounts of amide, basic, and non-basic nitrogen (probably largely, if not mainly, diamino- and monoamino-acids respectively) varied a good deal; the average amounts were approximately 24, 10, and 65 per cent. of the total nitrogen dissolved by boiling hydrochloric acid.

The nitrogen of the humus of these soils, extracted by 3 per cent. sodium hydroxide, varied, the average amount being about 62 per cent. of the total nitrogen. Of this, about 46 per cent. was precipitated by neutralising with acid, whilst an excess of acid gave a further precipitate containing about 12 per cent., so that a very considerable portion of the soluble nitrogen of these soils (42 per cent.) becomes soluble in acid after treatment with 3 per cent. alkali.

As regards other organic, non-humus substances present in soils,[13] benzoic acid has been obtained from a subsoil (but not from the corresponding surface soil), and *m*-hydroxytoluic acid has been found in several soils and subsoils, but only in any quantity in the latter. Vanillin, which had hitherto only been detected in soils by its odour and by some of its reactions, has now been isolated from some soils in Florida.

Aldehydes have been found in a number of soils—in neutral, alkaline, and acid soils, the latter containing aldehydes more frequently than the others. No relation seems to exist between the crop being grown and the presence of aldehydes, and they are not confined to any particular locality, being found as far apart as New York and Mississippi.

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[10] S. Odén, *Kolloid Zeitsch.*, 1914, **14**, 123; *A.*, i, 599; also *Arkiv. Kem. Min. Geol.*, 1914, **5**, No. 15; *A.*, i, 1165.

[11] J. A. Hanley, *J. Agric. Sci.*, 1914, **6**, 63; *A.*, i, 471.

[12] W. P. Kelley, *J. Amer. Chem. Soc.*, 1914, **36**, 429, 434, 438; *A.*, i, 368, 472.

[13] E. C. Shorey, *J. Agric. Research*, 1914, **1**, 357; *A.*, i, 916.

Both productive and unproductive soils were found to contain aldehydes; the majority of positive results were, however, obtained with unproductive soils.[14]

Partial Sterilisation of Soils by Heat and Antiseptics.

A study of the effect of various antiseptics on the numbers of bacteria in the soil, and on the production of ammonia,[15] showed that whilst the general effect of the different substances is the same, the amounts of the different antiseptics required to produce the same results vary considerably. As regards volatile antiseptics, the amounts required to produce the desired results were found to be as follows: toluene and carbon disulphide, 0·09; benzene, less than 0·16; *cyclo*hexane, 0·17; chloroform, 0·23; ethyl ether, 0·74; hexane, 0·86; methyl alcohol, 3·2; ethyl alcohol, 4·6 per cent. of the weight of soil. The action of non-volatile substances is more complex. Whilst cresol, for instance, produces the same initial effects on the number of bacteria as toluene, its subsequent effects are different in several ways; the number of bacteria increases enormously, and the flora is very simple as compared with that obtained when volatile antiseptics are employed. The high numbers are, however, not maintained, but fall rapidly. The increase in the ammonia is much less than with toluene. Phenol gives similar, and quinol (with only 0·05 per cent.) somewhat similar, results, whilst *p*-benzoquinone, although less potent, also behaves similarly. Both quinol and cresol seem to be utilised by the surviving bacteria as food.

Formaldehyde is normal in its initial behaviour, killing the protozoa and reducing the number of bacteria; this is followed by a marked rise in ammonia, but no increase in bacterial numbers. Pyridine has to be applied at the rate of 0·8 per cent., as smaller amounts are readily assimilated by the bacteria.

The results obtained with the various antiseptics on tomatoes grown in soils containing disease organisms showed that formaldehyde and pyridine are the most effective; next, cresol, phenol, calcium sulphide, carbon disulphide, toluene, benzene, and petroleum; whilst the least effective of the substances used are the higher homologues of benzene and naphthalene, and some of their derivatives. Steam proved, however, to be more effective than any of the substances mentioned, and in vegetation experiments a steamed soil should always be included as a standard. It must also be borne in mind that in laboratory experiments organisms, once killed, cannot reappear, whilst in culture experiments such rigid exclusion is, of course, impracticable, so that an absolutely identical order of effectiveness of the different antiseptics is not to be expected.

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[14] O. Schreiner and J. J. Skinner, *J. Franklin Inst.*, 1914, **178**, 329; *A.*, i, 1195.

[15] E. J. Russell and W. Buddin, *J. Soc. Chem. Ind.*, 1913, **32**, 1136; *A.*, i, 242.

The results of pot experiments[16] in which buckwheat, wheat rye, and barley were grown in a very poor loam which had been heated at 95°, 135°, and 175°, respectively, showed a marked acceleration of growth in the case of buckwheat in the soil heated at 95°; the other plants were only slightly affected. Heating at higher temperatures, especially at 175°, retarded germination and growth.

The results of other germination and vegetation experiments made in heated soils[17] indicated that a toxic substance is produced at low temperatures, and in greater amount at high temperatures, 125—150°. When low temperatures are employed, the effect of the toxin is not lasting, and the growing plant is eventually even benefited by the heating. The heated soils were found to contain more soluble inorganic, and especially more soluble organic, matter than before heating. When exposed to air, the toxic substance disappears, and much of the additional soluble organic matter reverts to its insoluble state. The production of a substance beneficial to plants, which is attributed to the oxidation of the toxin, might, however, equally well be due to the oxidation of some other substance present.

As regards the retarding effect of heating soils on germination, it has been shown[18] that ammonia has this effect, and that heated soils may contain ammonia in quantities capable of producing similar results.

In addition to changes in the solubility of humus brought about by heating soils, a number of experiments have been made with Hawaiian soils with reference to the changes in mineral constituents.[19] It is found that whilst the effects of heating vary with different soils, the amounts of water-soluble manganese, calcium, magnesium, phosphates and sulphates, and bicarbonates increase when soils are dried at 100°; in about half the soils, the solubility of the potassium, aluminium, and silica increases, whilst in some the solubility diminishes. Higher temperatures (250°) and ignition give similar results, the changes being sometimes greater and sometimes less than those produced at 100°.

Solubility in $N/5$-nitric acid was not altered much by heating the soils at 100°; heating at 250° in some cases considerably increased the solubility of the aluminium, manganese, potassium, and phosphoric acid, whilst calcium and magnesium became less soluble.

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[16] G. W. Wilson, *Biochem. Bull.*, 1914, **3**, 202; *A.*, i, 644.

[17] Duke of Bedford and S. P. U. Pickering, *J. Agric. Sci.*, 1914, **6**, 136.

[18] E. J. Russell and F. R. Petherbridge, *ibid.*, 1913, **5**, 248.

[19] W. P. Kelley and W. McGeorge, *Hawaii Exper. Stat. Bull.*, 1913, **30**; *A.*, i, 1044.

As regards nitrogen, the usual destruction of nitrates was observed, and ammonia was produced in abnormally large amounts; there was also a loss of about one-fourth of the total nitrogen when soils were heated at 200°. It was observed that when soils were subjected to the heat of brush fires, ammonification was stimulated, whilst nitrification was checked for at least two months. Hawaiian soils are characterised by inertness, and ploughing, followed by thorough tillage at frequent intervals for several months, is usually necessary; the burning of brush without aeration seems to have similar effects.

The action of lime in partly sterilising soils, to which reference was made last year, has been further studied, and a number of definite results relating to the changes in the number of bacteria, ammonification, and nitrification in a variety of soils has been obtained.[20] It is shown that the amount of lime required depends on the character of the soil. A sandy soil poor in organic matter and calcium carbonate required 0·2 to 0·3 per cent., a clayey soil containing calcium carbonate reacted with 0·3 to 0·4 per cent., whilst an acid, sandy soil, and a rich garden soil which contained calcium carbonate, required from 0·5 to 1 per cent.

The greatest increase in the number of bacteria was obtained in the acid, sandy soil. With 0·4 per cent. of lime, the number rose from 5 to 906 millions per gram in ninety days. The highest final number (337 millions after 310 days) was obtained with the same soil treated with 1 per cent. of lime. This soil also produced the highest amount of ammonia, 112 per million, as nitrogen, in 310 days, whilst the highest amount of nitric nitrogen was found in a humus-sandy soil, also with 1 per cent. of lime; this soil contained 210 per million of nitric nitrogen after 380 days.

The results of pot experiments in which different amounts of lime were added to the soil accorded with the nitrification results.

Results similar to these were obtained with a heavy soil containing calcium carbonate.[21] Addition of 0·3—1 per cent. of lime resulted in a marked decrease in the number of bacteria, followed by an immense rise, whilst 5 per cent. of lime completely checked bacterial growth. In a calcareous loam, addition of more than 0·05 per cent. of lime caused diminished nitrification, and on sandy soils, both rich and poor in calcium carbonate, addition of lime up to 0·1 per cent. lowered the production of nitrates from ammonium sulphate, and 0·5 per cent. inhibited nitrification.

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[20] H. B. Hutchinson and K. MacLennan, *J. Agric. Sci.*, 1914, **6**, 302.

[21] F. Miller, *Zeitsch. Gärungsphys.*, 1914, **4**, 194; *Bull. Agric. Intell. Plant Diseases*, 1914, **5**, 1168.

The effect of heat and of antiseptics on the catalytic power of soils, rate of the action of the soil on hydrogen peroxide, has been investigated.[22] As regards heat, it was found that in soils which have been heated at 100° the action on hydrogen peroxide is greatly reduced, and that a further reduction in the action is produced by heating at 250°. Treatment of the soils with mercuric chloride, phenol, and formaldehyde had no effect, except a slight diminution in the case of mercuric chloride, which is very difficult completely to remove. From these results the conclusion is drawn that the catalytic properties of soils are not essentially due to enzymes and microbes, but rather to colloids.

An investigation of the effects of toluene and carbon disulphide[23] applied to soils manured with cotton-seed meal and ammonium sulphate, respectively, showed that nitrification was not appreciably affected by about 0·1 c.c. of toluene per 100 grams of soil; larger amounts were injurious, and even inhibited nitrification for a time. The largest amount employed was 1 c.c. per 100 grams, and from the effects of this the soil recovered in about five months.

Carbon disulphide had no appreciable effect on the accumulation of nitrates except when more than 1·0 c.c. was added to 100 grams of soil. A temporary retarding effect was then produced, which, however, did not last long, even with 5 c.c. per 100 grams of soil.

Soils in which nitrification is inhibited for twenty weeks by large amounts of toluene or carbon disulphide may completely recover their nitrifying power without reinoculation.

A study of the development of Protozoa[24] in various media-ammonifying solutions containing bloodmeal, hornmeal and peptone, nitrifying solution, Giltay's denitrifying solution, etc., which were inoculated with soil, showed that a close relation exists between the development of Protozoa and that of the bacteria, the maximum activity of both corresponding very closely. This may be due to the Protozoa taking an active part in decompositions taking place; it seems, however, more probable that the Protozoa live on the bacteria, and this view is supported by the fact that the protozoal activity lags slightly behind that of the bacteria. This was very marked in the case of the nitrifying solution, in which the encystment of the Amœbæ was not complete until some days after the ammonia had disappeared.

Of the different Protozoa, the flagellates generally appeared first, and were almost immediately followed by the ciliates. These, after a prolonged period of activity, encyst, and are followed by the Amœbæ, which seem to prefer a medium containing few or no active Protozoa.

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[22] H. Kappen, *Bied. Zentr.*, 1914, **43**, 145; *A.*, i, 644.

[23] P. L. Gainey, *Centr. Bakt. Par.*, 1914, ii, **39**, 584; *A.*, i, 236.

[24] A. Cunningham and F. Löhnis, *Centr. Bakt. Par.*, 1914, ii, **39**, 596.

Practically the same fauna was found in each of the solutions employed, and an association of certain Protozoa with definite species of bacteria was, in the case of the Amœba, in the nitrifying solution.

As regards the effect of heat on active and encysted Protozoa, it is shown that the active forms are killed at 44—54°, flagellates being the least, and ciliates the most, resistant, whilst the cysts are killed at 70—72°. In the case of soils which cool more slowly than liquid cultures, it is considered probable that a temperature of 55—60°[25] would probably be as effective as 65—70° on solutions.

Ammonification, Nitrification, and Denitrification.

In order to ascertain the relative powers of various ammonifying organisms under different conditions, a series of experiments has been made in which three different soils were manured with four different nitrogenous substances, and inoculated with pure cultures of ammonifying organisms.[26] It was found that with the same organism the ammonifying power depends a good deal on the nature of both the soil and the manure, so that it cannot definitely be decided which, of the fifteen organisms used, is the best. On the whole, *B. tumescens* seems to be the most efficient. The highest efficiency with a manure was shown by *B. mycoides*, whilst with peptone *Sarcina lutea* gave the highest results. With dried blood and fish guano, *B. mycoides* showed only a moderate ammonifying power.

Taking ammonification as a criterion of availability, the results indicate that dried blood is inferior to fish guano and cottonseed meal.

Results of considerable interest have been obtained in an investigation on the nitrification of ammonium salts, the object of which was to ascertain what intermediate products are formed.[27] The experiments were made in filters, which were inoculated from actively nitrifying sewage filters. The compounds identified were hydroxylamine salts, which were estimated, and salts of hyponitrous and nitrous acids, and there was always some loss of nitrogen. The results are in accordance with the view that the process consists of successive hydroxylation of hydrogen atoms, and subsequent elimination of water. It is, however, not evident that

[25] E. J. Russell and H. B. Hutchinson, *J. Agric. Sci.*, 1913, **5**, 152.

[26] C. B. Lipman and P. S. Burgess, *Univ. Cal. Publ. Agric. Sci.*, 1914, **1**, 141.

[27] E. M. Mumford, *P.*, 1914, **30**, 36.

these initial changes were brought about by the nitrifying organisms, as a mixed culture was used. In any case, the results are of great interest.

That intermediate substances are produced by nitrifying organisms seems to be proved by a number of experiments which have been made on the rate of nitrification of ammonium salts and various organic compounds.[28] The substances were subjected to the action of a mixed culture of hydrolytic and nitrifying organisms obtained from the secondary contact beds of a sewage works. At short intervals the amounts of nitrogen as ammonia, nitrites, and nitrates were estimated. It was found that carbamide, uric acid, asparagine, glycine, methylamine sulphate, acetamide, ammonium oxalate, and sulphate all nitrify at about the same rate, and that the maximum amount of nitrogen recovered as nitrate was 95 per cent., owing, presumably, to losses by aeration and by the interaction of ammonia and nitrous acid.

The chief interest in these experiments is the temporary disappearance of nitrogen in the case of the ammonium salts. After fifty-seven days, only 57 per cent. of the total nitrogen of the ammonium sulphate added was present in the three forms, and 67 per cent. in the case of ammonium oxalate, indicating the presence of some compound intermediate between ammonia and nitrous acid, containing about 40 per cent., more or less, of the total nitrogen.

Thiocarbamide and aniline sulphate failed to nitrify. The latter substance is probably decomposed into ammonia and phenol, the phenol being at once destroyed by the bacteria; 90 per cent. of the nitrogen was recovered as ammonia.

In order to ascertain the influence of season and cultivation on the activity of soil bacteria, samples of soil, taken at intervals of about five weeks, were mixed with organic nitrogenous manures, and the rates of ammonification and nitrification determined.[29] As regards ammonification of such substances as meat, horn, and blood meals, there was a rise from August to October, then a tendency to fall in November, and a rise to a maximum in December. A minimum was reached in February, and a low maximum in April, followed by a slight fall to July, and probably August. The nitrification results were similar, except that the spring maximum was in March, whilst the fall commenced in April.

The variations in both ammonia and nitrates were slight, owing probably to the unusually mild winter, and the December maximum is attributed to the same cause.

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[28] R. M. Beesley, *T.*, 1914, **105**, 1014.

[29] H. H. Green, *Centr. Bakt. Par.*, 1914, ii, **41**, 577; *A.*, i, 1113.

In these experiments, the soil samples were taken both from a portion of the experimental field which had received autumn cultivation and from another portion which was not touched until ploughed in the spring. Although the crop results showed a superiority of 20 per cent. as regards nitrogen in favour of autumn cultivation, the bacteriological results failed to reveal any difference.

An investigation of the effects of irrigation and of crops on the nitrifying power of soils[30] showed that irrigation water caused a reduction in nitrification as indicated by laboratory experiments. The effects of crops varied both with the crop and the manure. Soil from lucerne land produced the greatest amount of nitrates from ammonium sulphate, whilst with dried blood, soil from the oat plots gave the highest results. The lowest nitrifying power, with both manures, was found to belong to the fallow plots, indicating that all the crops employed have a stimulating action on nitrification.

Comparing the soil samples taken at different depths, it is shown that about 90 per cent. of the nitrate found in the first 150 cm. of soil is produced in the top upper 45 cm.

A further study of the effect of crops and cultivation on bacterial activity[31] has been made with a considerable variety of soils, all of which, as frequently happens in the arid soils of Utah, contain plenty of mineral food and calcium carbonate, but not much nitrogen. It was found, in the first place, that cultivated soils contained about twice as many bacteria as the virgin soil, that it produced 30 per cent. more ammonia from dried blood, and twice as much nitric nitrogen as the virgin soil. Comparing the influence of the crops, it is shown that the lucerne soil produced much less nitrate than the wheat soil. Fallow soil which was hoed contained fewer organisms than the others, but their activity was greater, and their production of ammonia and nitrates higher than any of the others.

The results of anærobic experiments in which organic substances, such as peptone with meat extract, and peptone with dextrose, were inoculated with sewage filter humus[32] showed that half or more of the gas evolved was hydrogen, the rest being a mixture of nitrogen and carbon dioxide, varying in quantity according to the nature of the organic matter. When nitrates are added, no hydrogen is evolved, and there is a greatly increased liberation of nitrogen; a small amount of carbon dioxide is evolved, and a considerable amount of methane. Evidence was obtained that the production of nitrites is due to some enzyme secreted by the organism, the enzyme being again reduced to its natural state by the nascent hydrogen produced by the organism. The nitrates are then reduced to nitrogen by the action of hydrogen and carbon dioxide.

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[30] I. G. McBeth and N. R. Smith, *Centr. Bakt. Par.*, 1914, ii, **40**, 24.

[31] J. E. Greaves, *ibid.*, **41**, 444.

[32] W. Hulme, *T.*, 1914, **105**, 623.

Experiments with twenty-eight well-known, spore-producing bacteria showed that twenty of them reduce nitrates in the presence of dextrose, and seven others in the presence of peptone.[33] In some cases the nitrites produced seemed to have a toxic effect, which prevented their accumulation; in the presence of peptone, however, there was a considerable production of nitrites (up to 4 per cent. with *B. tumescens* and *B. subtilis*). Production of nitrites and ammonia is found to depend on the composition of the nutritive solution, and especially on its reaction, alkaline solutions, such as are obtained when peptone is used, being favourable to the production of nitrites, whilst with acid solutions, such as result from the employment of dextrose, ammonia is produced.

Experiments with *B. tumescens* showed that the whole of the nitrogen of the reduced nitrate, which was not in the forms of ammonia and nitrites, was assimilated by the bacteria. The conclusion drawn from these results is that the object of the reduction of nitrates is to utilise the nitrogen, and not the oxygen.

A number of ammonifying experiments, in which copper, zinc, iron, and lead sulphates were added to a sandy soil in amounts varying from 0·005 to 0·25 per cent., showed only relatively slight toxic effects; the action was generally more marked at concentrations below 0·1 per cent. than at those above that amount. No stimulation was observed at any concentration.[34]

Nitrification, on the other hand, was very considerably stimulated at the higher concentrations up to 0·15 per cent., except in the case of lead sulphate. At the lowest concentrations, 0·0125 per cent., the metals were either slightly toxic or without effect.

Whilst the addition of 4—6 per cent. of calcium carbonate to soil containing dried blood was found to increase ammonification, twice these amounts of calcium carbonate gave a smaller increase in the ammonia produced, and quite small amounts of magnesium carbonate (0·1 per cent.) retarded ammonification.[35] The same amount of magnesium carbonate completely inhibited nitrification; denitrification, on the other hand, was only retarded by larger amounts of magnesium carbonate.

The results, if confirmed, are of considerable interest. It seems evident, however, that an unexpected complication is introduced into vegetation experiments on the lime-magnesia ratio, especially as the addition of calcium carbonate seems to have no effect in diminishing the toxic action of magnesium carbonate on ammonifying and nitrifying organisms.

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[33] M. Klaeser, *Ber. deut. bot. Ges.*, 1914, **32**, 58; *A.*, i, 462.

[34] C. B. Lipman and P. S. Burgess, *Univ. Cal. Publ. Agric. Sci.*, 1914, **1**, 127.

[35] W. P. Kelley, *Bied. Zentr.*, 1914, **43**, 149; *A.*, i, 644.

In order to throw further light on the origin of the accumulations of nitrates in certain soils in Colorado and the neighbouring States, to which reference was made in previous Reports, the amounts of nitrates have been estimated in a number of shales, sandstones, and limestones of the old inland seas, as well as in alkali and in ash material collected in its original state.[36] The affected area, so far as is known, is within the section covered by the old Cretaceous and Tertiary seas, and it is found that large amounts of nitrates are present in the rocks of these formations, whilst the Jurassic shales and sandstones contain much less. The maximum amount of sodium nitrate in Cretaceous shales was more than 1 per cent., whilst alkali was found to contain as much as 3·35 per cent. The high local results are attributed to the low rainfall, and especially to the protecting covering of clay. Taking the average amount of sodium nitrate in fifty-eight samples as 0·104 per cent., it is calculated that the amount present in the Book Cliffs area in Utah and Colorado would be at least 90 million tons.

The results, along with those previously obtained, seem clearly to indicate that the nitrates of the affected areas are derived from the accumulations of ancient deposits.

On the other hand, evidence has been obtained, by means of nitrification experiments with Colorado soils, that not only the soils from areas in the incipient stage of sterility, but normal soils as well, have a very much greater nitrifying power than foreign soils.[37] The nitrifying flora of the Colorado soils seems to be distinct from that usually found in other soils, either consisting of quite different organisms or else of different strains. Whilst other soils produce the largest average yields of nitrates from dried blood, next from ammonium carbonate, and least from ammonium sulphate, with Colorado soils the order is reversed. Chlorides inhibit nitrification, whilst large amounts of nitrates seem to be without effect.

On the strength of these and previous results, showing the high ammonifying power which these soils were found to possess, and also the presence of algæ, chiefly *Nostocaceae*, for nitrogen-fixing organisms to feed on, the opinion that the high amounts of nitrates are derived from atmospheric nitrogen is maintained.

Whilst the theory that the nitrates are mainly derived from the deposits of the old inland seas seems the more probable for several reasons, the Colorado nitrifying organisms seem to be quite exceptionally active, and it would be interesting if they should prove to be related to Winogradsky's vigorous Quito organism. It has been suggested that the latter is descended from still more active microbes responsible for the Chile nitrate deposits.

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[36] R. Stewart and W. Peterson, *Utah. Agric. Coll. Exper. Stat. Bull.*, 1914, 134; *A.*, 1915, i, 51.

[37] W. G. Sackett, *Agric. Exper. Stat. Col. Agric. Col. Bull.*, 1914, 193.

Movements of Nitrates in Soils.

The observations made some time ago by Müntz and Gaudechon on the extreme slowness with which nitrates diffuse in arable soil have been confirmed by several experiments.[38] In sandy and clayey loam containing 13·5 and 16·8 per cent. of water, only relatively small amounts of nitrates diffused to a distance of 15 cm. in four months; a considerable diffusion in that time did not extend beyond 10 cm. Under practical conditions, diffusion is therefore comparatively unimportant, nitrates being carried down into the subsoil by rain, and again brought to the surface by capillarity. In a dry season, nitrates which were deposited at a depth of 25 cm. rose in eleven days to within 8 cm. of the surface, whilst nitrates deposited at a greater depth rose more than 40 cm. in a month.

In order to show the effect of the same amount of nitrates at different depths on the growth of beet, five small plots were arranged, in which the nitrate (500 kilos. per hectare) was applied at depths of 5, 10, 17, and 30 cm. respectively. The experiments also included an unmanured plot, and a similar series of plots without a crop. Estimations of nitrates in samples of the soils taken at different depths from April 15th to August 16th, and at different depths down to 40 cm., showed that on the fallow plots the effect of rain was to distribute the nitrates in the zone between 10 and 30 cm., and to increase the nitrates between 30 and 40 cm.; there was no loss of nitrates. As regards the beet plots, it was shown that the deep application of nitrates gave the best yield, owing to the better distribution of the nitrates. This is attributed to the upward movement brought about by the growing crop during the period of active vegetation, which seems to result in a better distribution than that caused by rain. It is therefore considered undesirable, as well as unnecessary, to apply the manure in instalments. This would not apply to a winter crop in a wet climate, when the advantages of autumn manuring with nitrates may be more than counterbalanced by losses.

A study of the amounts of nitrates in arable soils, based on the results of numerous estimations of nitrates in cropped and uncropped soils at different times of the year, showed that the amounts rarely exceeded 6 per million in sandy soil, 23 per million in loam, and 14 per million in clay soil.[39] These maximum amounts correspond, respectively, with about 30, 130, and 70 kilos. per hectare to a depth of 45 cm. The accumulation of nitrates was generally found to take place most rapidly in the late spring or early summer, after which the soils usually showed little, if any, gain in nitrates, and frequently a loss. In the hot, dry autumn of 1911, however, the accumulation went on in some cases until September.

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[38] L. Malpeaux and G. Lefort, *Ann. Sci. Agron.*, 1913, [iv], **2**, ii, 705.

Comparing different kinds of soils, it was found that the amounts of nitrates varied more on loams than on clays and sands. In clay soils, the winter losses were less; on the other hand, they accumulated smaller amounts in June and July.

Fallow soils were found to contain more nitrates than cropped soils in the late summer and early autumn, allowing for the amounts taken up by the crop. The rapid rise in the amounts of nitrates in the spring takes place, not immediately, but some time after the warm weather begins.

An investigation, in some respects similar to the one just referred to, has been made at Scania, in Sweden.[40] Nitrates were estimated at intervals of seven to ten days, to a depth of 30 cm., in the soil of a field on which different crops were grown successively from 1907 to 1911; from 1909, fallow plots were included. In the cropped soil, the amount of nitrogen as nitrates never exceeded 22 per million, whilst in the bare soil the maximum was 33 per million.

Comparing the amounts of nitrates in the plots under different crops, the maximum amounts of nitrogen were 14 per million in the case of beet, 8 to 9 per million with wheat and peas, whilst under grass the lowest results were obtained—1·5 per million. When, however, the grass was dug in, the nitric nitrogen rose to 6 per million, and by the middle of November to 21 per million. Application of dung resulted in vigorous nitrification, after which there was a fall in the amounts of nitrates, due partly to the wheat crop and partly to leaching by rain, so that by the spring the amount of nitrates in the soil was low. In the early summer there was again a rise, due to increased nitrification, and perhaps to a movement of nitrates from the subsoil upwards, which, however, was not maintained, owing to increased assimilation by the crop.

The effect of vegetation and tillage was shown by an experiment in which a grass plot was divided into three parts, one of which remained under grass, whilst the second was freed from vegetation, and the third dug to a depth of 30 cm. On the three divisions, the nitrogen as nitrates averaged, respectively, 2·4, 6·5, and 11·3 per million.

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[39] E. J. Russell, *J. Agric. Sci.*, 1914, **6**, 18; *A.*, i, 471.

[40] M. Weibull, *K. landtbr. Handl. Tidskr.*, 1914, **53**, 65; *A.*, 1915, i, 51.

In order to ascertain whether it is possible to detect the point at which nitrogenous manures become necessary, nitrates were estimated, during July and August, in eight unmanured plots under sugar-beet. The yields were estimated both on the unmanured and manured plots. Indications were obtained that where the nitrogen as nitrates fell to 2 per million by the end of July, applications of nitrogenous manures resulted in a fairly large increase in the yield, whilst with a later fall in the nitrates the effect of nitrogenous manure is less marked. Similar results were obtained with other crops. In an experiment with mangolds, where nitrogenous manure gave a large increase, the unmanured plot was found to contain only 2 per million of nitric nitrogen as early as June. The "critical" period will vary with different crops.

Toxins and Stimulants.

Reference has already been made to an organic substance found in an acid soil which is toxic to one kind of plant and stimulating to another; also to a toxic condition produced by heating soils, attributed to the formation of an organic toxin, but possibly due to ammonia, which, it is known, may be produced in sufficient quantity.

In connexion with the question of the production by plants of conditions inimical to succeeding plants, experiments with a variety of plants grown in sand showed that the second crop was considerably reduced, and that the third crop was further reduced.[41] The toxic action was not confined to plants of the same kind, but was manifested in the case of other plants. Similar results were obtained by adding to the sand roots grown in another pot. On the other hand, when the roots of the first crop were removed before sowing the second, the toxic effect was reduced somewhat, but was still very marked. Better results were obtained by washing the sand.

It is considered possible that the injurious effects may, in part, be due to the production of alkalinity, and it is shown that, of the plants employed, those which produce the greatest alkalinity (millet and camelina) suffer the most when the crop is repeated.

In accordance with the results of Whitney and Cameron, it was found that soil extracts frequently contained toxic substances which were, however, equally toxic to different plants. When the extract of a black soil was distilled, and both distillate and residue were employed for water-cultures, the growth obtained in the distillate was similar to that obtained in a normal solution, whilst the residue gave very slight growth. When the distillation was carried out under diminished pressure, growth in the residue was still more restricted. The toxicity of the soil extract is entirely removed by filtration through charcoal.

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[41] D. Prianischnikov, *Rév. Gén. Bot.*, 1914, **25**, 563; *A.*, i, 1208.

No toxic effect was observed when three successive crops of etiolated oats were grown in the same solution.

The injurious action of grass growing over the roots of fruit trees varies very considerably, according to the soil. On the shallow and not very rich soil of the Woburn Fruit Farm, which is on the Oxford clay, the effect is often fatal, whilst at Long Ashton, where the soil is rich and deep, the injurious action of grass is only slight. In the case of an old garden soil at Harpenden, no toxic action was observed.

The results obtained at Woburn[42] seem to exclude the possibility of the injurious effects of grass being due to differences such as the supply of water, alteration in the aeration of the soil, accumulation of carbon dioxide, alkalinity or acidity, etc., so that it seems probable that the action might be explained by the production of a toxin, either as a root secretion or, perhaps more probably, a decomposition product of the débris of the growing roots.

Experiments were accordingly made in which grass was grown over the soil in which the trees were planted, so arranged that whilst the grass roots were not in contact with the soil containing the tree, the leachings would reach the tree roots in a few minutes. Under these conditions, the same injurious effect was observed as when the trees and the grass shared the same soil. When, on the other hand, the grass is grown on trays away from the trees, and the leachings from the grass are exposed to the air for an hour or two before being applied to the tree, their action is no longer toxic, but beneficial.

The experiments were extended so as to include, instead of trees, a number of other plants, such as tobacco, tomatoes, and mustard, which received the drainage from clover; also *Festuca*, clover, mustard, and *Dactylis*, which received in each case leaching from plants of the same kind grown in trays over the pots. A reduction occurred in each case, varying according to the plant grown.

The beneficial effect of oxidised leachings, already referred to, is also obtained when the trays containing the grass are removed from the pots, provided this is not unduly delayed. If the plants have been injured beyond recovery, and hard-wooded plants soon become permanently stunted, no beneficial effect is, of course, to be expected.

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[42] Duke of Bedford and S. P. U. Pickering, *loc. cit.*

The conclusions drawn from these experiments are that a substance is produced from the roots of all crops, which is toxic to other plants, and still more so to plants of the same kind, and that when oxidised by air the toxin is converted into a stimulant. There is, however, no evidence that the stimulant is an oxidation product from the toxin rather than from some other constituent of the drainage.

It does not seem very clear why the leachings from the trays are injurious to the plants in the pots (presumably drainage from the pots would produce similar results if transferred to the trays) whilst it is without action, as soil solution, before it drains out of its own pot.

If it should be proved that the stimulant is formed by the oxidation of the toxin, and not from some other substance, then it follows that every growing crop results in the formation of a stimulant. In practice the stimulant might be expected to have more influence than the toxin, at any rate on arable land, since the toxin would no doubt be oxidised during the interval between the crops. For how long the stimulant resists oxidation remains to be ascertained.

A substance having considerable stimulative properties has been obtained[43] from peat which had been incubated with a mixed culture of aerobic organisms for two weeks. It was found, in the first place, that when seedlings of *Primula malacoides* were treated twice in six weeks with an aqueous extract of 0·18 gram of the peat, the plants grew to twice the size of other plants not so treated. Stimulative effects were next obtained with wheat seedlings by employing a solution of the residue of an alcoholic extract of the peat, and also the phosphotungstic acid precipitate from an aqueous extract of the same residue. At the end of five weeks, the plants which had been treated with the substance extracted by alcohol showed an increase of 21·1 per cent. over the check plants, which received only the complete plant food, whilst the pots which had been treated with the phosphotungstic acid precipitate gave an increase of 29·4 per cent. Experiments were then made to compare the effect of the phosphotungstic acid precipitate with that of the silver fraction corresponding with Funk's vitamine. In seven weeks the pot with the phosphotungstic acid precipitate showed an increase in dry produce of 22·7 per cent., and the silver fraction an increase of 17·7 per cent.

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[43] W. B. Bottomley, *Proc. Roy. Soc.*, 1914, [*B*], **88**, 237; *Ann. Bot.*, 1914, **28**, 531; *A.*, i, 1208.

Wheat seedlings in water-cultures with pure food solution alone gained in weight in ten days, after which there was a loss, resulting in a loss on original weight of 8·4 per cent. in fifty days. Addition of 0·35 per million of the silver fraction resulted in a continuous increase, and a final gain of 54·9 per cent. in the same period. Results similar to these were obtained with wheat seedlings from which the seeds had been removed.

No stimulating substance could be obtained from the original, untreated peat.

It is suggested that certain substances are formed during germination which enable the embryo to utilise the food supplied, and that, after the seedling becomes independent, some other source becomes necessary. The peat stimulant seems to be able to take the place of this substance in both stages of growth, and must, presumably, be formed during the usual humification processes in soils.

Whilst the stimulative effects of the substance from bacterised peat seem evident, the conclusion that the substance is not only a stimulant, but is essential, seems hardly justified, since it is possible to obtain fully-grown wheat plants in absence of any organic matter.

In vegetation experiments with toxic substance and stimulants, much depends on the methods employed, and it is evident that results obtained with water-cultures and in soils cannot be expected to agree closely. In water-cultures the plants are subjected to the action of the whole of the substance added, if not precipitated, whilst in soils the substance may not only be more or less absorbed, but may be expected to influence the bacteria as well as the plants, so that, in addition to the direct toxic or stimulative effect, as the case may be, on the plant, an indirect action in the same direction, or possibly reversed, due to action on the soil organisms, is not at all unlikely.

The results of water-culture experiments with different substances indicate that plants are better able to resist the action of injurious substances in summer than in spring or winter.[44] The highest indifferent amounts of zinc sulphate vary, according to the season, between 0·2 and 0·04 mg. per litre in the case of barley, and between 0·2 and 0·05 mg. with peas. Arsenious acid and arsenites are found to be more toxic, especially with peas, than arsenic acid and arsenates. Boric acid is less toxic than zinc and arsenic, being injurious only when the amount exceeds 10 parts per million.

No stimulating effect has been observed with zinc and arsenic at any concentration down to 0·005 mg. per litre in the case of zinc, and 0·02 mg. with arsenic acid. Boric acid, at the rate of 10 parts to 0·05 parts per million, has a stimulative effect on peas; in the case of barley, the appearance of the plants seems to indicate stimulation, but this is not confirmed by the weights of the produce.

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[44] W. E. Brenchley, *Ann. Bot.*, 1914, **28**, 283; *A.*, i, 790.

In pot experiments with wheat grown in soil,[45] it is shown that zinc salts applied in quantities up to 0·1 per cent. have a stimulating effect, especially on the production of straw, which shows very considerable gains. Larger amounts are toxic. Of the different salts employed, the nitrate proves to be more active than the carbonate or phosphate.

Copper, as sulphate, applied at the rate of 0·01 to 0·02 per cent., has a stimulative action, whilst larger amounts are toxic and smaller amounts without effect. With manganese phosphate and carbonate, and cerium oxide and sulphate, the results are negative.

In an unproductive, sandy loam, which did not respond well to general manures, the application of four different manganese salts and the dioxide resulted in every case in an increased yield.[46] Stimulation varied, however, both with the salt and with the amount added. The best results were obtained with 50 parts per million of the chloride, which increased the yield by 31 per cent. The smallest gains were obtained with manganese carbonate and dioxide.

On the whole, applications of 25 to 50 parts per million, corresponding with 14 to 28 kilos. per hectare, gave the best results.

Very different results were obtained with a productive clay loam. In this soil, manganese failed to show any appreciable increase with any manganese salt; sometimes there was a slight depression.

Further experiments on the growth of wheat in aqueous extracts of different soils showed that addition of manganese salts had similar effects. In extracts of poor, unproductive soils, manganese salts increased growth and the oxidising power of the roots. In extracts of productive soils, oxidation was again increased, whilst the growth was diminished. The conclusion drawn from these results is that the beneficial action in unproductive soils is due to increased oxidation resulting in the destruction of toxic substances in the soil. In productive soils, injury may result from excessive oxidation.

The results of a field experiment on an acid, clay loam showed that all of the five crops grown were injured by manganese salts, and that the oxidising power was reduced. Failure is, in this case, attributed to acidity.

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[45] J. A. Voelcker, *J. Roy. Agric. Soc.*, 1913, **74**, 411; *A.*, i, 1192.

[46] J. J. Skinner and M. X. Sullivan, *U.S. Dept. Agric. Bull.*, No. **42**, **1914**; *A.*, i, 1196.

Other experiments with manganese salts have been made, some of which indicate that only small amounts can be applied with advantage,[47] whilst according to others the amounts required are so large that it is doubtful whether the use of manganese salts can be remunerative.[48] This divergence is no doubt due to the different characters of the soils.

Alkali salts have both toxic and stimulative actions, according to the concentration, on the germination and growth of rice.[49] The maximum stimulation was obtained with $N/500$-solutions in the case of magnesium sulphate, with $N/1000$—5000 in the case of magnesium and alkali chlorides, whilst with sodium sulphate, chloride, and carbonate the maximum stimulation was with $N/50$—100-, $N/100$-, and $N/100$—500-solutions, respectively. Most of the salts were toxic in concentrations above $N/100$. When, however, two of the salts, even in $N/10$-solutions, are mixed in suitable proportions, the toxic action of each is more or less completely overcome. This is mainly due to the antagonism of the cations, the antagonism of the anions being relatively feeble. It is also shown that bivalent cations are strongly antagonistic to univalent cations, but that univalent cations do not very markedly antagonise bivalent cations.

Neither barium nor strontium can take the place of calcium in counteracting the toxic action of sodium and manganese salts; barium increases the injury, if anything. In mixtures of three salts, all of which are toxic at the concentrations employed, growth is generally better than in two of them.

Plant Nutrition and Manures.

Fixation of nitrogen by *Azotobacter* is found to be greater when mixed cultures of different strains are employed than with pure cultures of the same bacteria.[50] The presence of humus, even in considerable amounts, seems to have no unfavourable effect on nitrogen-fixation, and small amounts of sodium nitrate have very little effect. When, however, the amount of nitrogen as nitrate exceeds 2·5 per cent. of the carbon present, fixation of nitrogen is retarded, or checked altogether. As regards the effects of different forms of nitrogen, humus gives positive results, whilst with humus from green manure negative results are obtained.

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[47] O. M. Shedd, *J. Ind. Eng. Chem.*, 1914, **6**, 660; *A.*, i, 1164.

[48] T. Pfeiffer and E. Blanck, *Landw. Versuchs-Stat.*, 1913, **83**, 257; *A.*, i, 243.

[49] K. Miyake, *J. Coll. Agric. Tohoku Imp. Univ.*, 1914, **5**, 241.

[50] J. Hanzawa, *Centr. Bakt. Par.*, 1914, ii, **41**, 573; *A.*, i, 1113.

These results seem to show that in natural soils fixation of nitrogen can only in very exceptional cases be retarded by the nitrogen compounds present. Nevertheless, the amount of nitrogen fixed in this manner, in ordinary arable soils, must be comparatively insignificant, and soils which contain high amounts of organic carbon and nitrogen, from repeated applications of dung, soon lose much of their carbon and nitrogen when manuring is discontinued. This has been found to occur even when the crop grown is clover, which in a purely mineral medium, without combined nitrogen, leaves a considerable nitrogenous residue.

The results of field experiments, in which oats were manured with sulphur, showed that no beneficial effect was obtained, the yields being, if anything, slightly depressed.[51] Pot experiments in which mustard, rape, and clover received sulphur at the rate of from 3·4 to 13·4 kilos. per hectare, gave negative results.[52]

It has been observed in the case of wheat grown in the absence of silica that plants which were attacked by rust suffered severely, the rust spreading very rapidly.[53] It is accordingly suggested that cereals grown on dolerite and basalt soils should suffer less from attacks of this kind than when grown on granite soils, provided that the climate and the weather conditions are the same.

The losses in nitrogen to which farmyard manure is subjected when stored may be due to the washing out of soluble substances by rain, to volatilisation of ammonia, and to the form of denitrification, in which nitrogen is liberated, which might perhaps be better termed deazotisation, to distinguish it from denitrification without loss of nitrogen.

It has been shown [54] that, of the three processes, the first is much the most important to be avoided. A manure heap exposed to rain for three months not only lost 24 per cent. of its nitrogen, but more than 20 per cent. of the dry matter as well. In six months the losses rose to more than 34 and 31 per cent. respectively, and there was also a loss of 8 per cent. of the phosphoric acid.

By keeping a heap under cover, the losses of dry matter and nitrogen were reduced very considerably, and no phosphoric acid was lost at all. In a heap which was sheltered from rain, but kept moist by watering, the loss of nitrogen was doubled as compared with the unwatered heap; there was, however, no very appreciable increase in the loss of dry matter.

Apart from the washing out by rain, the relative importance of the losses by volatilisation of ammonia, and by the complete

[51] T. Pfeiffer and E. Blanck, *Landw. Versuchs-Stat.*, 1914, **83**, 358; *A.*, i, 469.

[52] J. A. Voelcker, *J. Roy. Agric. Soc.*, 1913, **74**, 419; *A.*, i, 1196.

[53] M. Lundie, *South African J. Sci.*, **9**; *Chem. News*, 1914, **110**, 200; *A.*, i, 1192.

[54] E. J. Russell and E. H. Richards, *J. Bd. Agric.*, 1914, **21**, 800.

reduction of nitrates, must depend a good deal on the weather conditions. With a succession of showers, with intervals of dry weather long enough to give the maximum production of nitrates at the surface, losses by denitrification would be very considerable. That, no doubt, is what happened in the watered heap referred to, but, on the whole, it is considered more likely that the greater loss will usually be in the form of ammonia.

A new potassium manure has been prepared from leptite or curite, a common rock in Central Sweden.[55] The mineral, which contains up to 11 per cent. of potash, is heated with coal and iron filings in an electric oven, with carbon electrodes, at about 1800°. In this manner a slag is obtained, which consists chiefly of potassium and aluminium silicates, 90 per cent. of the potassium being soluble in hot 20 per cent. hydrochloric acid. As compared with potassium sulphate, the results of pot experiments, in which the same amounts of potassium were supplied in the two forms, showed that the "electro-potash," as the new manure is called, yielded 78 per cent. of the crop obtained with potassium sulphate.

From experiments made in the United States, it has been estimated that a million tons of potassium chloride per annum could be obtained from seaweed.[56]

Methods.

Of the papers dealing with methods of importance in agricultural laboratories may be mentioned those on the estimation of carbohydrates in plant materials,[57] a colorimetric method for nitrites and nitrates,[58] methods for estimating acidity and carbonates in soils,[59] and a modification of König, Hasenbäumer and Hassler's method for estimating the surface of soils.[60]

N. H. J. MILLER.

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[55] H. G. Söderbaum, *Kungl. Landtbr.-Akad. Handl. Tidskr.*, 1914, **53**, 15.

[56] "Production et Consommation des Engrais Chimiques dans le Monde." Rome, 1914.

[57] W. A. Davis and A. J. Daish, *J. Agric. Sci.*, 1914, **6**, 153; *A.*, ii, 588; A. J. Daish, *ibid.*, 255.

[58] E. A. Letts and Miss F. W. Rea, *T.*, 1914, **105**, 1157.

[59] H. B. Hutchinson and K. McLennan, *Chem. News*, 1914, **110**, 61; *A.*, ii, 784; *J. Agric. Sci.*, 1914, **6**, 323.

[60] J. A. Hanley, *J. Agric. Sci.*, 1914, **6**, 58; *A.*, ii, 312.

MINERALOGICAL CHEMISTRY.

Although the year has not been marked by any outstanding discovery serving to open up an entirely new field of research, the progress to be noted along the familiar channels may be considered to be more than satisfactory. A short appreciation of the general tendencies may fitly precede a discussion of the work in detail.

The *X*-ray methods of investigating crystal structure have naturally received much attention, both on the part of continental workers, who appear to be chiefly attracted by the more theoretical aspects, and also by W. H. and W. L. Bragg, who, in a series of brilliant experimental researches, have succeeded in unravelling the structure of several elementary and compound substances. Certainly the most striking feature of the work is the remarkable degree of intimacy to which these authors have carried their structural dissections. They have not been merely content to familiarise us with the general nature of crystal structure, but have carried their explorations to the utmost limit of chemical interest, namely, the atoms. The further development of this absorbingly interesting field of work must surely throw light on many questions now in dispute; in particular, its application to the simpler cases of polymorphism may well be expected to accelerate a decision between the present conflicting theoretical views.

There has been a very marked activity in the province of chemical crystallography proper. The foundation by Fedorov of the method of crystallochemical analysis very materially enhances the value of a crystallographic description, proving, as it does, that any substance which has once been measured can be readily identified on any subsequent occasion, and without involving the slightest loss of any valuable material. The brief accounts of two cases in which a crystallographic identification of several products was quite indispensable to the successful issue of a biochemical research will, perhaps, convince the most hardened Philistine that crystal-gazers have occasionally their lucid intervals in which they may be of some use to the more wideawake of their chemical brethren. Among the more conventional pieces of work, the investigations of Wahl are, perhaps, pre-eminent as being valuable contributions to our knowledge of the crystalline form of substances which are liquids, or even gases, at the ordinary temperature. On the theoretical side, there has been a dignified interchange of opinion between Richards and Barlow and Pope on the chemical aspects of the valency volume theory.

The systematic physico-chemical investigation of mineralogical problems continues to make very obvious advances, especially in the hands of the American geophysical school. Bowen's masterly investigation of the ternary system, diopside–forsterite–silica, shows both a clear appreciation of the difficulties to be overcome and a nice discrimination of the methods which are the most likely to make for success. The research may be upheld as a model which other workers would do well to copy. The exact petrological information that is already beginning to accrue from such investigations is in itself a sufficient repayment for all the trouble involved. Another important work from the same school is that of Fenner on the various polymorphous modifications of silica; a significant feature of this work is the astounding sluggishness of certain polymorphous transformations, which may be used as an argument in favour of polymerism.

The last general topic to be discussed is the problem of "liquid crystals." Few subjects have ever awakened the general interest aroused by the discovery of these much-discussed substances by Otto Lehmann; there was a time when it was impossible to attend a conversazione without being asked to give an account of their properties, or, in default, to swell the audience of a colleague's demonstration. It is therefore not surprising that the general interest soon began to flag. A new stage was, however, inaugurated by the chemical researches of Vorländer, who prepared a vast number of new examples in a high state of purity, and also added considerably to the general stock of knowledge, showing that the production of the turbid liquid phase is a constitutional feature of a peculiar type of stereochemical configuration. It was, however, reserved for a pure physicist, Bose, to lay the foundation of a general theory of "anisotropic liquids," and to substantiate his theory by means of a carefully planned series of experiments. It is indeed fortunate that these experiments, so untimely interrupted by Bose's early death, have been continued by others. Mauguin's electromagnetic researches, in particular, afford a very striking confirmation of Bose's views. Again, the definite proof that the cubic modification of silver iodide does not in reality form liquid crystals is very suggestive as indicating that a molecular configuration of some chemical complexity is indispensable to a regular orientation of liquid molecules. It is perhaps only to be expected that Lehmann should find a difficulty in adapting himself to the new views, however much the new researches add lustre to his discoveries. The history of liquid crystals affords a good example of the rapidity with which a scientific enigma may be compelled to give up its secret when once it has attracted the attention of a number of differently equipped workers. The writer believes that these Reports will have conspicuously failed in one of their main objects if they do not serve to stimulate a more catholic interest and in a small measure help the specialist to take up a less detached attitude towards science as a whole.

X-Ray Methods of Exploring Crystal Structures.

The progress made in this branch of investigation has already reached a stage at which the relative merits of the reflection and diffraction methods may be appraised. The rapid advances made by the users of the *X*-ray spectrometer[1] are to a large extent due to the simplicity of the method involved. The various glancing angles, θ_1, θ_2, θ_3, etc., at which a plane of atoms serves as an efficient reflector, are first determined, and the results are then interpreted by means of the equation $n\lambda = 2d \sin \theta$. In this equation the factor n has the value 1 when the reflection is due to a mutual reinforcement of pulses provided by successive chemically and crystallographically identical planes (first-order reflection at the angle θ_1). Similarly, the co-operation of alternate planes leads to the second-order reflection, θ_2 ($n=2$), the mutual assistance of every third plane to the third-order reflection, θ_3 ($n=3$), and so on. The intensity of the reflection diminishes regularly in passing up the orders, except in cases where successive atomic planes differ either as to composition or to their distances apart; even orders may become stronger than odd orders, and certain orders may vanish altogether. An admirable illustration of these effects is given by rock salt, the relative reflection intensities from the cube and octahedral planes being:

	1st order.	2nd order.	3rd order.	4th order.
Face (100) ……	100	18·7	6·25	too weak to measure
,, (111) ……	16·5	24·4	3·1	4·2

The regular decrease of intensity as the scale of orders is ascended indicates both a chemical identity and an equality of spacing of successive cube planes, whilst the periodical rise and fall of intensity in the octahedral plane premises some structural peculiarity or other. A glance at the figure given in last year's

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[1] W. H. Bragg, *Phil. Mag.*, 1914, [vi], **27**, 881.

Report will reveal the fact that successive cube planes are identical in every respect, whereas octahedral planes are alternately occupied by chlorine and sodium atoms. An example in which an "order anomaly" has necessarily to be referred to a difference of spacing is afforded by the diamond (p. 243); in this case the entire absence of the second-order reflection from the octahedral plane immediately led to the correct elucidation of the peculiar and highly interesting structure involved.

The diffraction method of exploring crystal structure is, of course, based on the production of a Laue radiogram, by placing a crystal in the path of a primary pencil of *X*-rays and receiving on a photographic plate both the undeviated pencil and the secondary, deviated beams which are due to the diffraction or reflection effect of the internal planes of the crystal. An analysis of the radiogram is then made both with respect to the pattern and the relative intensities of the spots.

A cursory examination of the published material is enough to show that the employment of the Bragg *X*-ray spectrometer leads to a rapid determination of the general features of a particular structure, and in the simpler cases may even obviate any appeal to the evidence afforded by the Laue radiogram. On the other hand, although an unaided analysis of the radiogram is apt to lead to inconclusive and even erroneous results, it cannot be denied that it not only serves as a check on the spectrometric method, but also brings with it an additional quantitative precision in the finer details. This point will be emphasised under pyrites and hauerite (p. 246). It is obvious, then, that the two methods admirably supplement one another.

An important contribution is that of Friedel,[2] who has pointed out that the radiogram does not admit of a decision as to whether a crystal is endowed with a centre of symmetry. An immediate result of this is to rule out any hope of obtaining direct evidences of enantiomorphism, and the announcement in last year's Report, for example, of a difference between *d*- and *l*-crystals of quartz, must accordingly be withdrawn. A useful table of the theoretical symmetry types of radiogram is appended by Friedel, from which it appears that the thirty-two classes of crystal symmetry can only yield a total of eleven types. In the cubic system, for instance, the holohedral, holoaxial, and tetrahedral classes are indistinguishable radiographically, all yielding a holohedral pattern, but the tetartohedral and pyritohedral classes must both afford the pyritohedral type. This deduction, as far as pyrites is concerned, has been fully confirmed. The keen disappointment felt by crystallographers when it was first announced that the undoubtedly tetrahedral zinc blende yields a holohedral radiogram must now be tempered by the knowledge that no other result could in the nature of things be expected.

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[2] G. Friedel, *Compt. rend.*, 1913, **157**, 1533.

The year has been characterised by a considerable amount of work, and apparently of quite a fundamental character as far as physics is concerned, on the Debye effect[3]—the influence of temperature on the atomic vibrations in the crystal edifice. It is interesting to note that Debye's theory has received a qualitative confirmation.[4] An obvious diminution in the intensity of the secondary beams is exhibited by mica when it is kept at a temperature of 400°, and spots that are faintly visible at the ordinary temperature are not at all represented on the photograph. Again, there is no trace whatsoever of any spots when X-rays are passed through a crystal of rock salt heated at 620°. The spectroscopic method also indicates a weakening in intensity of reflected rays with rise of temperature; moreover, the increase of the value d, owing to the general expansion of the crystal (rock salt), is clearly indicated by a corresponding diminution of the glancing angle, θ, a result which is to be expected from the form of the reflection equation.

X-Ray spectra have been mapped out by de Broglie[5] by the following ingenious device. Rays are allowed to impinge on a crystal which is mounted on a spectrometer, rotated by clockwork at a rate equal to 10° per hour. An intense reflection of rays is thereby produced, and is registered on a photographic plate, at each short interval of time during which the glancing angle has a value satisfying the reflection equation $n\lambda = 2d \sin \theta$. Since both plate and anticathode are kept fixed throughout the experiment, the point of impingement of the reflected rays gradually moves across the plate, and the latter, on development, reveals the spectrum as a series of bands and lines with great definition. The spectrum appears to range over several octaves.

Stereochemical Deductions from the X-Ray Methods of Investigation.

We may now proceed to review in detail those crystalline substances the structures of which have been elucidated with a reasonable degree of certainty. In addition to those now discussed, there are a certain number of others, amongst them being sulphur and quartz,[6] which are admittedly imperfectly characterised; and the same is perhaps true for the calcite group of minerals and sodium nitrate, although the results already obtained vindicate the closest structural analogies which have ever been claimed for these substances. It seems advisable to postpone discussion of such cases until additional evidence is available.

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[3] Various papers in *Physikal. Zeitsch.* and *Ann. Physik.*

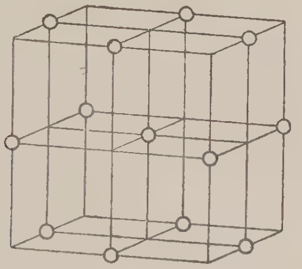
[4] M. Laue and J. St. van der Lingen, *Physikal. Zeitsch.*, 1914, **15**, 75.

[5] M. de Broglie, *J. Phys.*, 1914, [v], **4**, 101.

[6] W. H. Bragg, *Proc. Roy. Soc.*, 1914, [*A*], **89**, 575.

Copper.[7]—Although in point of time the latest to be investigated, it is convenient to make a commencement with this element, since the structure proves to be the simplest of all crystals so far examined. In spite of this structural simplicity, however, the actual exploration was accompanied by considerable experimental difficulties, owing to the softness of the material, which renders it very susceptible to profound structural derangements when attempts are made to grind artificial planes with appropriate crystallographic orientations. This difficulty was finally surmounted by etching away the external layers so as to lay bare the unimpaired structure. The results unhesitatingly point to an arrangement of atoms on the pattern of the centred-face cube shown in Fig. 1. This arrangement corresponds with the closest packed cubic arrangement of equal spheres, and with a rhombic dodecahedral domain of influence for each copper atom.

FIG. 1.



Diamond.[8]—The main structural peculiarity of the diamond is the tetrahedral environment of each carbon atom by its four immediate neighbours, a feature which is obviously of prime stereochemical significance. In the absence of a model, the real nature of the structure is perhaps best realised by the following construction. Take eight small cubic cells, four being empty, whilst the remaining four are of the kind shown on a large scale in Fig. 2, that is, provided with a whole carbon atom, 2, at the centre, and a quarter of an atom at each of four corners, numbered 1, 6, 7, 8, selected tetrahedrally. Now interpose the two kinds of cells in the way shown in Fig. 3, so that the occupied cells are identically orientated, but separated from each other by the empty cells. It is seen that four quarter-atoms now meet at the centre of the figure numbered 1, and thus make up a whole atom. (It need scarcely be added that an infinite repetition of the eight cells throughout space would lead to a similar fourfold completion of all the quarter atoms, so that the assemblage consists in its entirety of whole atoms.) An imaginative chemist will doubtless see clear evidences of a six-carbon ring—shown, as to five atoms, by, say, 7, 2, 1, 3, 9—and may accordingly be disposed to trace an embryonic benzene configuration in the structure. Without laying too much stress on this point, it will be generally agreed, in view of the perfect tetrahedral environment of all the atoms, that the diamond structure can be regarded as a perfect symbol of the chemistry of carbon.

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[7] W. L. Bragg, *Phil. Mag.*, 1914, [vi], **28**, 355; *A.*, ii, 775.

[8] W. H. and W. L. Bragg, *Proc. Roy. Soc.*, 1914, [*A*], **89**, 277.

In addition to its four immediate neighbours at the distance $\sqrt{3}.a/2$, where a denotes the edge-length of the cubelet, each carbon atom is symmetrically surrounded by twelve other atoms at the somewhat greater distance $\sqrt{2}.a$. These twelve atoms have to be taken into account in any determination of the sphere of influence of each atom. It has been pointed out by Föppl[9] that the sphere of influence is accordingly a regular tetrahedron, each of the four corners of which has been modified by the dodecahedron to such an extent that the original triangular faces of the former are cut away to regular hexagons. Inasmuch as this modified tetrahedron deviates considerably from the form of a sphere, it is evident that the diamond structure corresponds with an extremely loose-packed system of spheres. This peculiarity has led Barlow[10] to offer the opinion that X-ray methods may be incapable of correctly de-

FIG. 2.

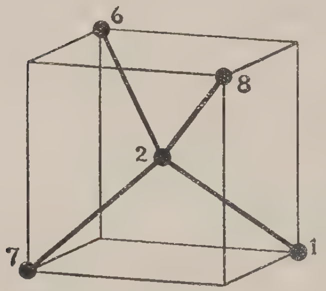
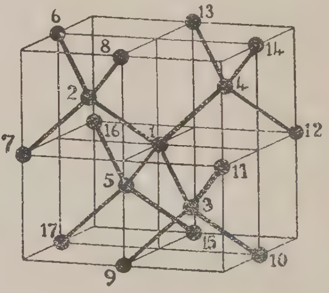


FIG. 3.



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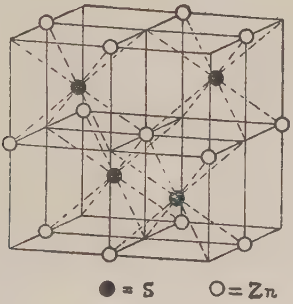
[9] L. Föppl, *Physikal. Zeitsch.*, 1914, **15**, 191.

[10] W. Barlow, *Proc. Roy. Soc.*, 1914, [*A*], **91**, 1; *A.*, ii, 843.

ciphering the intimate structure of crystals, and to propose certain modifications which might tend to bridge the apparent gulf between the requirements of the Barlow-Pope theory and the experiments of W. H. and W. L. Bragg.

Although in the past the many crystallographical and physical aspects of the diamond have been the subject of repeated inquiries, it cannot be said that the results obtained are altogether satisfactory. Thus, the frequent twinning on the cube plane would seem to negative the structural subsistence of a corresponding plane of symmetry, the effect of which would be to relegate the crystal to the tetrahedral class. This tetrahedral symmetry would, however, in turn imply electric polarity along the trigonal axes; the recent exhaustive work of van der Veen,[11] however, failed to trace any such polarity. The stereochemical elucidation of the diamond appears to have furnished a satisfactory answer to these contradictions;[12] the cube planes of the structure are not planes of symmetry, nor are the trigonal axes polar, for although successive octahedral planes of atoms are alternately spaced at distances in the ratio 1 : 3, the structure is nevertheless identical when viewed along the trigonal axes in opposite directions.

FIG. 4.



Zinc Blende,[13] ZnS.—The atomic arrangement in this mineral is precisely analogous to that of the foregoing, and it is therefore only necessary to suppose the quarter atoms on the cube corners to be composed of zinc, whilst the central atoms are sulphur. The structure indicated in Fig. 4 is thus obtained. Although the arrangement of the material is obviously the same, the difference in composition brings about a fundamental structural difference as compared with the diamond, for successive octahedral planes are now strewn with zinc and with sulphur atoms respectively; the trigonal axes are now polar, and the symmetry of the assemblage corresponds exactly with that of the mineral. It will be seen that each zinc atom is tetrahedrally surrounded by four sulphur atoms, and more distantly by twelve other zinc atoms. It must be added that a careful analysis of the original Laue radiograms now corroborates Bragg's structure in every detail.[12]

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[11] A. L. W. E. van der Veen, *Zeitsch. Kryst. Min.*, 1913, **51**, 545.

[12] P. P. Ewald, *Ann. Physik*, 1914, [iv], **44**, 257.

[13] W. L. Bragg, *Proc. Roy. Soc.*, 1914, [*A*], **89**, 468; *A.*, ii, 181.

Fluorspar,[13] CaF_2.—The structure of this substance has also been investigated by W. L. Bragg, and apparently with satisfactory results. The atomic arrangement advocated may again be visualised by the construction adopted for the diamond and zinc blende. In the latter assemblage, substitute F for S, and Ca for Zn, so that each of the four occupied cubic cells corresponds with a group –CaF. In order to make up an assemblage corresponding in composition with CaF_2, it is obviously necessary to allocate an additional number of fluorine atoms; if each of the four empty cube cells of the diamond and zinc blende structures be now supposed to contain a centrally situated fluorine atom, the assemblage of Fig. 5 is finally obtained. The symmetry of the assemblage corresponds with the holohedral cubic class, and is in agreement with all available crystallographic knowledge.

Fig. 5.

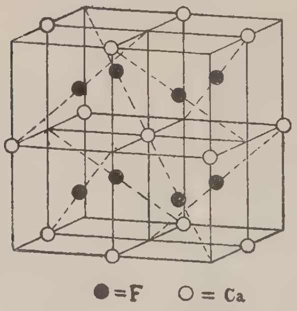
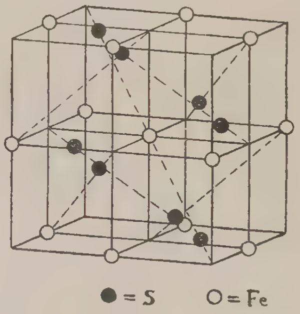


Fig. 6.



Iron Pyrites,[13] FeS_2, *and Hauerite,* MnS_2.—The geometrical form and physical properties of these two isomorphous minerals are so replete with items of interest as to warrant an expectation that the underlying structure should also offer unique peculiarities. This expectation has been conspicuously realised, for Bragg's analysis, effected by the help of the *X*-ray spectrometer, proves the intimate atomic structure to be in accordance with one of the Fedorov-Schönflies point systems, namely, the asymmorphous system $(25)x'$ of Fedorov's classification.[14] Moreover, a detailed analysis and comparison of the radiograms obtained by Ewald serve to fix the relative spacing of the iron (or manganese) and sulphur atoms with great precision.

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[14] E. S. Fedorov, *Zeitsch. Kryst. Min.*, 1914, **54**, 163.

The structure is represented in Fig. 6. It betrays a general similarity to the structure adopted for fluorspar, but the following important difference must be noted: each sulphur atom is not situated at the centre of its cubic cell, but has been moved along an appropriate cell diagonal away from an iron atom towards an unoccupied corner, so that its distance from the iron atom is about four times its distance from the unoccupied corner. It will be observed that the displacements of the sulphur atoms are not along a series of parallel diagonals, but rather according to a definite scheme in which the various diagonals are favoured in turn. The symmetry of the structure is in complete harmony with that of the crystal. Preliminary experiments carried out with crystals of hauerite also led to the same general conclusions.

The publication of these results furnished Ewald[15] with an indispensable foundation for the exhaustive analysis of Laue's radiograms. This analysis proves the essential correctness of Bragg's deductions, the sole modification being that in hauerite the position of the sulphur atom is obtained by dividing the cube diagonal in the exact ratio 4:1, whilst in pyrites the sulphur is a little nearer to the metallic atom than Bragg supposed, the corresponding ratio being 7:2.

It may be mentioned, in concluding this section. that a valuable appreciation of the recent advances in stereochemical crystallography has been contributed by Groth,[16] who concludes that regularities, like the symmetrical environment of each sulphur atom in zinc blende by four zinc atoms, must be held to indicate that no sulphur atom is specifically united to any single zinc atom in the chemical sense, and it must therefore be inferred that chemical molecules do not exist in the crystalline condition. The writer believes this conclusion to be not a little premature. Although the frequent formation of crystalline double salts, like the alums, clearly proves that crystallisation is accompanied by a certain amount of pooling of chemical affinities, it must nevertheless be apparent that to deny the existence of the chemical molecule would open up most extensive possibilities of isomeric change, optical inversions, and so forth, whenever the crystalline structure is broken down by dissolving or fusing the substance, Such changes have never been observed. The reader need hardly be reminded that X-ray methods of investigation are still in their infancy, and that, however remarkable the progress already made, it must be strongly emphasised that all theoretical interpretations must be regarded as provisional. Happily, the originality of the workers who are devoting themselves to the study of this new branch of investigation is in itself a sufficient guarantee, not only that steady progress will be made, but also that entirely new developments may be expected.

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[15] P. P. Ewald, *Physikal. Zeitsch.*, 1914, **15**, 399.

[16] P. Groth, *Zeitsch. Kryst. Min.*, 1914, **54**, 65 ; *A.*, ii, 719.

Crystallo-chemical Analysis.

The trustworthiness of Fedorov's method of identifying a substance by virtue of its characteristic crystalline form has been put to a further searching test, with results that demonstrate its extremely practical value to the chemist. The following two examples taken from a brochure written by Fedorov[17] will be enough to show that the method can be successfully applied even when the available amount of material will not admit of a chemical analysis.

In a research on the chemical processes that accompany the ripening of seeds, N. R. Nedokuschaev was seriously impeded owing to the small quantities of the products isolated. The latter he eventually handed over to M. B. Orelkin and G. Pigulevski, pupils of Professor Fedorov, in order to see whether crystal measurements would afford any clue to the identity of the substances, and the crystal analysts succeeded in identifying asparagine, $C_4H_8O_3N_2$; allantoin, $C_4H_6O_4N_4$; histidine, $C_6H_9O_2N_3$; arginine, $C_6H_{14}O_2N_4$; and betaine, $C_5H_{11}O_2N$. Of these compounds, histidine was identified in the form of its hydrochloride and betaine as platinichloride.

The same chemical crystallographers rendered inestimable assistance to A. A. Pomaski in a research on the teleutospores of the rust fungus (*Puccinia graminis Persoon*), and identified *d*-mannitol, $C_6H_8(OH)_6$, and "vitaline." The latter substance belongs to the class of the crystalline albumens, and according to Weyl has the composition $C=52{\cdot}43$, $H=7{\cdot}12$, $N=18{\cdot}1$, $S=0{\cdot}55$, $O=21{\cdot}8$ per cent. Its molecular weight is unknown. The amount of vitaline placed at the crystallographers' disposal was 0·05 gram, and was found to be quite sufficient.

It is evident that the method is destined to be of a special value to the bio-chemist, and it is therefore desirable that every well-crystallised substance of complex chemical structure should be goniometrically measured, its geometrical form properly analysed, and its characteristic constants tabulated. It may be stated that the immense work connected with the tabulation of the thousands of substances which have been measured and described by successive generations of crystallographers is drawing to a satisfactory conclusion, the tables being already in the proof stage. A discussion of some of the points arising out of the study of these tables has been recently given by Fedorov,[18] and the quickest methods of measuring a crystal and tracing its identity by means of the tables has also been described by the creator of the method.[19]

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[17] "Crystallochemical Analysis" (Russian), 1914.

Crystal Symmetry and Molecular Symmetry.

The exceedingly rapid development of stereochemical ideas since the enunciation of the tetrahedral hypothesis of carbon by van't Hoff and Le Bel would lead one to suppose that the possibility of the existence of a close connexion between molecular and crystal symmetry must have occurred to the minds of many workers. As far as published material goes, the credit of the first examination of this subject appears to belong to the veteran mineralogist Tschermak, who, in 1903, pointed out certain numerical regularities, now known as "Tschermak's rules," that subsist between the general composition of a substance and the form or symmetry of the crystal. Thus, the formulæ Al_2O_3,$NaNO_3$, $NaIO_3$,$3H_2O$, in which the number 3 constantly recurs, represent well-known cases of rhombohedral or trigonal crystals; $ZrSiO_4$,SnO_2, tetragonal; $MgSnF_6$,$6H_2O$, hexagonal; CBr_4, cubic; and so on. Several contributions to the same subject have been published during the last ten years, and have received due notice in these reports, so that it only remains to give an account of some recent notable developments.

The general relationship between crystal symmetry and molecular symmetry has been discussed by Fedorov,[20] who with all modesty puts forward the conception of a crystal-molecule, consisting of n chemical molecules, where $n=1$ in the exceedingly rare case in which the symmetry of the chemical configuration corresponds exactly with the symmetry of the crystal. If, on the other hand, the molecule is completely asymmetric, and the crystal form is, say, rhombic sphenoidal, the number $n=4$; more generally, if p represents the "symmetry magnitude" of the crystal, m the symmetry magnitude of the molecular configuration, then $n=p/m$. It will be observed that the possibility of the chemical symmetry being greater than the crystal symmetry is not considered; Fedorov believes it to be mathematically impossible, which is perhaps another way of stating that the assumption is contrary to the dictates of common sense. It will be readily realised that in those cases in which the symmetry of the chemical formula is incompatible with the observed symmetry of the crystal, there must be an error somewhere—if not in the crystal determination, then in the chemical formula. One or two cases are discussed, and chemists are advised to set to work on the congenial task of devising new formulæ.

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[18] E. S. Fedorov, *Zeitsch. Kryst. Min.*, 1914, **53**, 337.

[19] *Ibid.*, 1914, **54**, 17; *A.*, ii, 718.

[20] *Ibid.*, 1913, **52**, 22; *A.*, 1913, ii, 305.

Any discussion of a chemical formula obviously implies, or leads up to, a discussion of the valency, and, stereochemically, the symmetry of the atom. The main result of Fedorov's analysis is that carbon amongst the quadrivalent elements, and aluminium amongst the tervalent elements, exhibit the clearest, although not perfect, crystallochemical evidences of a symmetrical disposition of the chemical valencies. Those who peruse Fedorov's paper will no doubt come across one or two statements of doubtful cogency; in particular, the reporter does not see why the bromine atom in $CBr(C_6H_5)_3$ and the hydrogen atom in CHI_3 are "certainly devoid of a threefold axis of symmetry."

The same problem, at least as far as carbon is concerned, has been attacked by Wahl,[21] who, with rare experimental skill, has not only succeeded in determining the crystal system of some forty carbon compounds which are liquids or gases at the ordinary temperature, but also the system of crystallised argon and nitrogen! The determinations were, of course, carried out optically. Argon and nitrogen are optically isotropic, and presumably belong to the cubic system. In the case of carbon compounds, there is a moderately general agreement between the symmetry of the crystal and the symmetry of the molecular configuration; for example, both methane and its tetrasubstituted derivatives, CBr_4, CI_4, $C(NO_2)_4$, and CMe_4, are cubic; the disubstituted products, CH_2Cl_2, CH_2Br_2, CH_2I_2, are rhombic, and the trisubstituted derivative, iodoform, and also ethane are hexagonal. The author accordingly draws the conclusion or "theory" that "the symmetry of the chemical molecule of a substance determines its crystal symmetry." The author is aware that some of the compounds examined will not fit in with the theory unless the usual spacial formulæ are arbitrarily deformed to correspond with the observed determinations. For example, methyl chloride, bromide, and iodide are monoclinic. These irregularities the author seeks to explain by means of certain ideas on the magnitude of atomic spheres of influence, but these explanations are, of course, only paraphrases of the anomalies, and do not in any way restore the generality of the theory. A valuable research which bears on the subject is that of Drugman,[22] who has made an extensive study of certain symmetrical dibasic, aliphatic acids. Thus, malonic, glutaric, dimethylmalonic, diethylmalonic, $\beta\beta$-dimethylglutaric, $\alpha\alpha'$-dihydroxy-$\alpha\alpha'$-dimethylglutaric, and n-pimelic acids should all presumably crystallise in the rhombic system. In reality, however, the respective systems of crystallisation are triclinic, monoclinic, tetragonal (trapezohedral), triclinic, monoclinic, triclinic, and monoclinic.

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[21] W. Wahl, *Proc. Roy. Soc.*, 1912, [*A*], **87**, 371; 1913, [*A*], **88**, 34; 1913, [*A*], **89**, 327; 1914, [*A*], **90**, 1; *A.*, 1912, ii, 1044; 1913, i, 693; 1913, ii, 1031; 1914, ii, 348.

[22] J. Drugman, *Zeitsch. Kryst. Min.*, 1914, **53**, 240; *A.*, i, 140.

Attention may here be drawn to a study[23] of a suite of four isomeric dinitrobenzoic acids, and also to an exhaustive examination of a series of monosubstituted benzoic acids.[24] Certain morphotropic relationships are discussed in the latter paper, but a careful perusal of the memoir shows that the allocation of indices is of a pronounced subjective character, and is directly responsible for some of the alleged morphotropic similarities.

The Barlow-Pope Theory.

An interesting and illuminating discussion on its merits and shortcomings has taken place between the authors of the theory and Richards.[25] The chief bone of contention is the question as to the compressibility of atoms. It is well known that the American chemist has from time to time adduced a large amount of experimental evidence in favour of atomic compressibility,[26] whilst on the other hand the propounders of the theory would seem to find no difficulty in elucidating crystal structure without having recourse to any such assumption. Perhaps the most important point made by Richards is the proof that Le Bas' interpretation of a volume relationship, $C=4H$, is inconclusive, since alternative assumptions that $C=2H$ or $3H$ or $5H$ will fit in equally well with the known molecular volumes of the paraffin hydrocarbons concerned.

The theory has also been described by Pope in his Presidential Address to Section B at the Australian meeting of the British Association; although no new matter is introduced, this contribution will be found to be a useful outline of the present position held by the propounders of the theory.

The practical development of the theory has been actively prosecuted during the year in a series of papers constituting numbers V—VII of "Morphological Studies of Benzene Derivatives," in which an enormous number of new crystal measurements are described and discussed in the light of the theory.[27] In addition to crystal measurements, the seventh memoir contains an account of observations on the principal magnetic directions of a number of monoclinic crystals, which were carried out in the hope that they might provide critical criteria for the correct setting of crystals. If by the term "correct setting" the authors imply the same meaning as Fedorov, it would seem that they have omitted to take into consideration the fact that magnetic induction is an ellipsoidal property, and on that account is entirely useless for the end in view. The authors' general conclusion is that their work provides a verification of the Barlow-Pope conception of valency volume.

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[23] B. Gossner, *Zeitsch. Kryst. Min.*, 1914, **53**, 489; *A.*, i, 406.

[24] H. Steinmetz, *ibid.*, 463; *A.*, i, 405.

[25] T. W. Richards, *J. Amer. Chem. Soc.*, 1913, **35**, 381; 1914, **36**, 1686; W. Barlow and W. J. Pope, *ibid.*, 1675, 1694; *A.*, 1913, ii, 483; 1914, ii, 719.

[26] T. W. Richards, *ibid.*, 1914, **36**, 2417.

Thermal Studies of Minerals.

Considerable developments have taken place during the year in the study of the equilibrium conditions of mineral mixtures, and as marked progress has to be noted both in the methods of working and in the actual results obtained, it will be convenient to divide the short résumé into two sections.

Methods.

Whenever feasible, it is best to measure temperatures by means of a platinum–platinum-rhodium thermo-element. The methods of constructing, calibrating, and using this invaluable form of thermometer have been recently described in a series of papers dealing with calorimeters and thermo-electric instruments of precision by White.[28] The experimental error varies with the amount of material taken and the character of the contact between the element and the mineral charge. With a careful worker the error may fall as low as ±2°. The limit of applicability appears to lie at about 1600° (the melting point of platinum is 1755°). For higher temperatures recourse must be had to far less accurate methods; it is therefore fortunate that the great majority of minerals melt below 1600°, the only exceptions being a few oxides and sulphides which have long been known to be highly refractory materials.

Since the direct observation of the melting point, as, for example, by means of the Doelter heating-microscope, must always remain a cumbrous and quite untrustworthy procedure owing to the difficulty of seeing whether a viscous mass is solid or liquid, it has been necessary to devise indirect or non-visual methods. The earlier method employed by the American workers was to raise the temperature of the crucible at a regular rate by means of an electric source of heat, and plot temperature-time curves; any absorption of heat, whether due to liquefaction or to a polymorphous change, brings about a decrease in the rate of the rise of temperature. It must be noted that the converse method, namely, that of cooling curves, is untrustworthy owing to supercooling effects. A second and later method, and one which is now extensively employed, is that of "quenching."[29] The crucible is kept at a constant temperature for an hour or so, and then suddenly quenched by dropping it into a dish of mercury. This sudden cooling transforms any molten material into glass, the presence of which is immediately recognised by a subsequent examination of the product under the polarising microscope. By trying successive temperatures at 5° or 10° intervals, the temperature at which glass is first formed is thus discovered. By trying higher temperatures, the point may then be determined at which the whole of the crucible contents, after quenching, proves to take the form of glass. The two points thus discovered are the solidus and liquidus temperatures for the given mixture. It is obvious that the microscopic examination also leads to the identification of the various crystalline phases which are in equilibrium with the fusion.

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[27] H. E. Armstrong, R. T. Colgate, and E. H. Rodd, *Proc. Roy. Soc.*, 1914, [*A*], **90**, 111; C. S. Mummery, *ibid.*, 455; H. E. Armstrong and E. H. Rodd, *ibid.*, 463; *A.*, ii, 443; i, 1062; ii, 768.

[28] W. P. White, *J. Amer. Chem. Soc.*, 1914, **36**, 1856, 1868, 2292, 2313; *A.*, ii, 767.

Another point that has been subjected to a searching examination is the all-important question of the condition of the material under investigation. It goes without saying that this material should be chemically pure; the silicates employed have therefore to be made artificially from pure silica and metallic oxides. Now, although it is an easy matter to obtain a product of a definite composition, it is extremely hard to ensure that it shall consist of a single chemical species. Suppose, for example, it is desired to prepare a series of pure magnesia-lime pyroxenes ranging in composition between diopside, $CaMg(SiO_3)_2$, and clino-enstatite, $MgSiO_3$. It is not sufficient to fuse together the correct proportions of lime, magnesia, and silica and allow the mass to cool, for in systems which are characterised by the separation of mixed crystals, the liquidus has not the same composition as the solidus, and crystallisation is accompanied by a gradual impoverishment of the liquid portion in one or more of the components. It is impossible to keep down the rate of cooling to such an extent as to allow a perfect attainment of true equilibrium conditions. Theoretically, the first crop of mixed crystals should redissolve as the temperature is lowered, if solid and liquid were in perfect equilibrium; in practice, the final crystalline product must always be extremely variable from point to point throughout the mass. The obtainment of homogeneous equilibrium material is of great importance, especially when it is to be used for subsequent researches. The only way to obtain it is to quench the fused pyroxene to a homogeneous glass, and then maintain this glass for some time at a temperature which is just a little below the point at which it commences to liquefy. The homogeneous glass then crystallises to a conglomerate of homogeneous mixed crystals.

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[29] N. L. Bowen, *Amer. J. Sci.*, 1914, [iv], **38**, 207 ; *A.*, ii, 772.

Results.

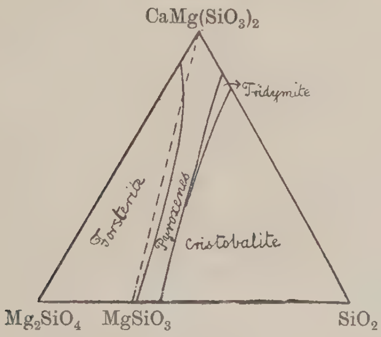
Binary System,[30] $MgO-SiO_2$.—This system, which has been carefully determined by Bowen and Andersen, is characterised by the appearance of two well-defined compounds—the orthosilicate forsterite, Mg_2SiO_4, and the metasilicate clino-enstatite, $MgSiO_3$. The latter substance was on a previous occasion shown to occur in four polymorphous forms, to which a fifth ("α-$MgSiO_3$") was added somewhat later; it is now pointed out that this fifth form is optically identical with forsterite, and owes its origin to the dissociation of clino-enstatite at its reputed melting point into the orthosilicate and free silica: $2MgSiO_3 \rightleftarrows Mg_2SiO_4 + SiO_2$. The main features of the system may be epitomised as follows: Magnesia (periclase) has a very high melting point, perhaps 2800°, and forms an eutectic (1850°) with forsterite, which itself melts at 1890°. There is no eutectic between forsterite and clino-enstatite; the eutectic between the latter and cristobalite (silica) lies at 1543°. Cristobalite melts at 1625° or higher.

Ternary System,[29] *Diopside–Forsterite–Silica.*—Although the scope of this system only extends over three-eights of the system $CaO-MgO-SiO_2$ the most important portion of the latter is really included, for the part under consideration embraces the pyroxene and olivine families of minerals. The quenching method was employed, the material used being a previously prepared series of lime–magnesia metasilicates to which appropriate amounts of pure forsterite or silica were added. The exact temperature needed for complete liquefaction and also the identity of the phase which was the last to disappear (or, alternatively, the first to reappear when the temperature was slightly lowered) were determined for each mixture. Such results are best illustrated by a space model constructed on a triangular base so as to allow of an exact representation of the relative concentration of the three components, the vertical dimension being reserved for temperature. In a case like the present, in which the three components do not form a continuous series of solid solutions, the top of the model (see Fig. 7)

[30] N. L. Bowen and O. Andersen, *Amer. J. Sci.*, 1914, [iv], **37**, 487; *A.*, ii, 562.

will be divided by boundary curves into a number of fields or areas, each representing the fusion surface of a solid phase. In the case in point there are four such fields: forsterite, pyroxenes, cristobalite, and tridymite, the latter area being very circumscribed. Two important points may be noticed with regard to the pyroxenes: (1) the area extends uninterruptedly from diopside across the whole of the diagram, thus indicating the existence of a complete series of mixed crystals ranging from $CaMg(SiO_3)_2$ to $MgSiO_3$; (2) the boundary line, forsterite–pyroxene, crosses the dotted line, $MgSiO_3$–$CaMg(SiO_3)_2$, at a point corresponding with about 70 per cent. of diopside, from which it follows that all metasilicate fusions, excepting those very rich in lime, will at the commencement of crystallisation deposit forsterite (olivine). Pyroxenes will only appear when the silica-enrichment of the liquid residue brings its composition to the forsterite–pyroxene boundary.

FIG. 7.



If the cooling is sufficiently slow, the originally deposited forsterite will then commence to dissolve in the silica originally liberated; if, however, the rate of cooling does not admit of the attainment of equilibrium, the forsterite will remain permanently, and the excess of silica will eventually crystallise out. We have here an elegant explanation of two petrological enigmas: (1) the not infrequent occurrence of olivine in the presence of free quartz; (2) the unmistakable signs in many rocks of a gradual resorption of olivine with the production of pyroxene. Again, the zonal development of pyroxenes generally shows a preponderance of magnesia in the nucleus. This is what would be expected from Bowen's work, since the magnesia pyroxenes have higher melting points than the lime pyroxenes. The paper includes amongst other important matters an extensive series of optical determinations of the whole series of pure lime–magnesia pyroxenes.

Polymorphism.

Since it is generally agreed that two or more materials of the same percentage composition must always be regarded as "polymorphous modifications" until definite experimental evidence necessitates the employment of different formulæ, it is obvious that the term polymorphism can only be defined in negative chemical terms. The history of chemistry abounds with numerous proofs that the polymorphs of yesterday are the isomerides of to-day: as chemical means of detecting differences of structure have become more and more refined the more imposing has become the list of instances in which polymorphous modifications have finally received the hallmark of chemical respectability. Especially resisting to this civilising influence, however, are the old stock cases of polymorphism in which the physical differences are satisfactorily interpreted as merely due to a different space-lattice arrangement of the same chemical molecule. The interpretation is sufficient because there is no evidence of any persistence of the characteristic physical differences when once the crystal structure is broken down; it must hold the field until such time as chemical differences have been proved by tests or reactions applied in the crystalline state. It is, however, very questionable whether the chemistry of the solid condition has yet seen the light of day; if in truth it has, the infant must indeed be preternaturally silent.

One of the consequences of the rapid growth of physical chemistry has been the increasing tendency to apply physical evidence as a means of attacking such chemical problems as present insuperable experimental difficulties when approached in more orthodox ways. In the abstract, this is all to the good, but in practice there must always remain a doubt as to how far any such physical considerations have any real chemical bearing. This remark appears to be particularly relevant to Tammann's "atomic theory of polymorphism."[31] Tammann believes that certain cases of polymorphism are to be regarded as simply due to a space lattice rearrangement, whilst others result from chemical polymerism. The criterion to be applied in the discrimination between the two categories is to study the stability relationships of the polymorphs over an extended range of temperature and pressure, and in this way discover whether the two forms can co-exist in stable equilibrium under varying conditions. According to Tammann, stable coexistence implies polymerism, whilst cases, in which one form is entirely metastable with regard to the other, are deemed to be instances of a space lattice rearrangement. The results of an examination of some thirty organic compounds lead Tammann to the conclusion that most cases of polymorphism belong to the latter category. Ice, however, is held to be a notable exception. Although the five forms of ice, which are now known as a result of the careful work of Bridgman,[32] would be regarded as examples of polymerism, a sixth form (the so-called modification III′), which Tammann has recently added to the list,[33] is, according to the same authority, to be regarded as a space lattice rearrangement of the form III. Bridgman[34] is, however, of the opinion that III′ is not merely metastable, but has no existence whatever. With regard to the validity of his physical criterion, Tammann adduces certain thermodynamical considerations in its support, but Smits[35] is of the opinion that the process of reasoning amounts to putting a preconceived idea into the thermodynamical machine and subsequently extracting the same after a respectful interval.

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[31] G. Tammann, *Zeitsch. physikal. Chem.*, 1913, **82**, 172; *A.*, 1913, ii, 193.

Of an entirely different nature is Smits's[36] theory of dynamic polymorphism (or "allotropy"). Polymorphism is held to be in itself a definite indication of the existence of more than one chemical species, and the two (or more) isomerides are supposed to co-exist both in the fused substance and in the various polymorphous modifications in a state of dynamic equilibrium. If the two forms are denoted by A and B, then fall of temperature is accompanied by a steady shifting of the equilibrium in the sense, $A \longrightarrow B$. The transition temperature is held to be the point at which one crystal structure will not allow of any further change, $A \longrightarrow B$; accordingly, a new space lattice structure of a more accomodating nature makes its appearance. By way of criticism, it is only necessary to recall and contrast the perfect limpidity of all polymorphous modifications with the turbidity that invariably accompanies any serious contamination of any crystalline substance with another (even if the contamination be isomorphous), to see that Smits's theory can scarcely commend itself to the pure crystallographer; but, however this may be, it must be stated that the theory has served to interpret a considerable number of curious facts. The theory can be invoked,[37] for example, in order to interpret the fact that the melting point of rhombic sulphur varies with the temperature at which the specimen has been previously maintained. It is true that the observed temperature difference only amounts to about 0·5°, but in the case of the polymorphous forms of silica, to be described presently, certain temperature fluctuations have been observed, according to circumstances, in the values of one of the transition points, and these variations are not so open to doubt, at any rate on the score of minuteness.

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[32] P. B. Bridgman, *Proc. Amer. Acad.*, 1912, **47**, 441, 558; *Zeitsch. anorg. Chem.*, 1912, **77**, 377; *A.*, 1913, ii, 39.

[33] G. Tammann, *Zeitsch. physikal. Chem.*, 1913, **84**, 257; *A.*, 1913, ii, 935.

[34] P. B. Bridgman, *ibid.*, 1914, **86**, 513; *A.*, ii, 254.

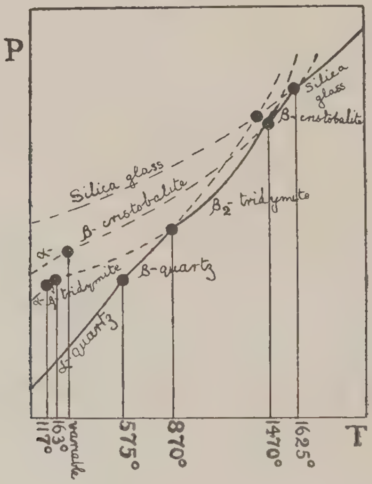
[35] A. Smits, *ibid.*, 1913, **82**, 657; **84**, 250; *A.*, 1913, ii, 393, 933.

[36] *Ibid.*, 1911, **76**, 421, and various subsequent papers.

[37] *Idem.*, *ibid.*, 1913, **83**, 221; *A.*, 1913, ii, 499.

Fenner's Work on Quartz, Tridymite, and Cristobalite.[38]—The transition temperatures and general conditions of stability of the numerous modifications of silica are indicated in Fig. 8, in which the experimentally determined temperatures are plotted against theoretical (imaginary) vapour pressures, all that is implied being that the curves express the general experimental work. It will be observed that each mineral species exists in at least two modifications (α and β). Now Fenner found the change $\alpha \rightleftarrows \beta$ to differ from a change of one mineral species into another in the following important particular: the former takes place rapidly immediately a transition temperature is overstepped, whereas the latter change is excessively slow. Quartz, tridymite, and cristobalite can co-exist together without undergoing any serious transformation at all, except at very high temperatures; and in order to determine these transition temperatures it was found necessary to add a small amount of sodium tungstate, which apparently exercises a catalytic function. The same stubborn persistence of metastable phases is also characteristic of the devitrification of silica glass, and even in the presence of sodium tungstate the first crystallised product is

FIG. 8.



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[38] C. N. Fenner, *Amer. J. Sci.*, 1913, [iv], **36**, 331.

generally a metastable one. Fenner is therefore driven to the conclusion that the extreme slowness of the changes, quartz tridymite $\rightleftarrows$ cristobalite, demands the assumption that each is a different chemical species. It is then possible to refer the sluggishness of each transformation to the time demanded by processes of polymerisation and depolymerisation. On the other hand, the two kinds of quartz (α and β) are supposed to be composed of the same chemical molecules, the transformation being due to a slight modification of the crystal lattice; and the same is true for the three tridymites (α, β_1 and β_2). The cristobalites, however, exhibit the following curious behaviour: the transformation point $\alpha \rightleftarrows \beta$ is extremely variable and depends entirely on the previous history of the specimen. The higher the temperature at which it was originally obtained from amorphous silica, the higher is the observed transition temperature; α-cristobalite changes into β-cristobalite at temperatures which range regularly between the limits 220—274°, according as the original temperature of its formation had a low or high value between the limits 1050—1600°. Fenner holds that this behaviour points to the co-existence in cristobalite of two kinds of material in the sense of Smits's theory, the idea being that if the equilibrium condition between the dynamic isomerides responds very slowly to a change of temperature, then the relative amounts in a given specimen will depend on its past thermal history.

The interpretation of the quartz and cristobalite inter-relationships, based on the work of Endell and Riecke,[39] has been independently undertaken by Smits and Endell.[40] They conclude that the behaviour of α- and β-quartz and cristobalite is referable to the existence of two kinds of chemical molecules, the relative amounts of which can be indicated by arranging the minerals in the order: α-cristobalite, β-cristobalite, β-quartz, α-quartz.

Relationships like those subsisting between α- and β-quartz, in which the two forms are extremely similar in optical properties and apparently only differ in symmetry, have long been known amongst laboratory products. An excellent example of this "polysymmetry" has been described during the present year.[41] Above a temperature of 18°, butyranilide crystallises in the rhombic system, but the crystals are pseudotetragonal. On allowing the specimen to remain, a gradual equalisation of the angles takes place, so that after a period of eighty-five days, the crystals have become truly tetragonal. On raising the temperature, the reverse progress gradually sets in. The tetragonal form may be obtained directly by keeping the crystallisation solution below 10°.

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[39] K. Endell and R. Riecke, *Zeitsch. anorg. Chem.*, 1912, **79**, 239; *A.*, 1913, ii, 134.

[40] A. Smits and K. Endell, *ibid.*, 1913, **80**, 176; *A.*, 1913, ii, 318.

[41] C. T. R. Wilson, *Proc. Roy. Soc.*, 1914, [*A*], **90**, 169.

The work described in a previous Report [42] on the formation and stability relationship of pyrites and marcasite, FeS_2, and zinc blende and wurtzite, ZnS, has been considerably extended.[43] The method employed in the estimation of the relative amounts of pyrites and marcasite was that originally due to Stokes; this method has been carefully examined, and found to be entirely trustworthy when certain precautions are observed.[44]

Anisotropic Liquids or "Liquid Crystals."

The important observation of Reinitzer that cholesteryl benzoate melts at 140° to form a turbid, doubly refracting liquid, which, at a temperature of 179°, becomes clear and singly refracting, prompted Lehmann to undertake an extensive microscopic study of the substance. Gattermann's syntheses of *p*-azoxy-anisole and -phenetole, as also the preparation of several other compounds by other workers, soon led to a considerable augmentation of the available experimental material, and it was not long before Lehmann drew the conclusion that such turbid liquid phases are to be regarded as aggregates of "liquid crystals." It is well known that suggestions that the liquids are really emulsions were soon proved to be untenable.

One cannot but infer from a close perusal both of the early and of the most recent books and memoirs, which have been so lavishly written by Lehmann, that he has always been at least as much swayed by certain, peculiar theoretical considerations, as by his actual observations. If the term crystal connotes a homogeneous mass of material, arranged on a space-lattice pattern, it is obviously no light matter to put a fluid mass to the proof of experiment; for many of the tests to which a crystalline medium characteristically responds are wholly or partly inapplicable, owing to this very fluidity: any attempts to investigate elasticity, cohesion, or cleavage are quite unthinkable. The general optical properties, on the other hand, are certainly more hopeful, and it is in the field of microscopic work that Lehmann has made most valuable observations. At the same time, however, it must be emphasised that the possession of properties like double refraction and dichroism does not prove the liquid substances to be crystalline; it merely indicates the existence of a definite regularity of struc-

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[42] *Ann. Report*, 1912, 266.

[43] E. T. Allen, J. L. Crenshaw, and H. E. Merwin, *Amer. J. Sci.*, 1914, [iv], **38**, 393; *A.*, ii, 850.

[44] E. T Allen and J. L. Crenshaw, *ibid.*, 371; *A.*, ii, 850.

ture of some kind or other, and exactly to that extent, and no further, supports an analogy between them and crystals. It may be noted that Lehmann, who is naturally never more clear-sighted than when he is criticising the views of others, is himself fully aware that optical evidence can never be regarded as complete: apropos, Vorländer's assertion that his viscous substances must be regarded as uniaxial crystals because they exhibit a perfect uniaxial interference figure, Lehmann states[45]: "such a liquid mass can only be regarded as a uniaxial liquid crystal provided it strove during its growth to attain a square or six-sided outline." Now, as a matter of fact, it is just this evidence that one seeks for in vain in Lehmann's own published writings. Although the diagrammatic drawings originally given for ammonium oleate are clearly hexagonal bipyramids,[46] it is, nevertheless, stated in the text that the outlines are really circular "owing to surface tension," and this admission is, of course, fully borne out by the photographic reproductions. In Lehmann's latest book[45] the diagram no longer indicates any hexagonal character, whilst in a quite recent memoir[47] there is even a mention of the form being that of a tetragonal bipyramid. Perhaps the clearest geometrical shapes of all are shown by Vorländer's *p*-azoxybenzoic ester; but even in this case, as far as one can judge from a photograph, the elongated shapes are due to a linear aggregation of more or less globular individuals, producing a segmentation effect.

The cubic modification of silver iodide occupies an altogether exceptional position in the history of liquid crystals. It is only in recent years[45] that Lehmann has given a new interpretation of his early work on this substance and has claimed it to be the first known example of liquid crystals—because "it is impossible by mechanical means to prove the existence of an elasticity limit," which means that silver iodide at high temperatures becomes so soft that it can no longer be regarded as a solid. Some remarkable researches on this point have been published during the year.[48] It has been shown that if every precaution as to chemical purity is employed in the preparation and subsequent handling of the substance, it is much harder at 550°, that is, 2° below its melting point, than is yellow phosphorus at the ordinary temperature. The addition of a small quantity of ordinary silver iodide immensely increases its plasticity. Since similar results were obtained by the same authors with silver chloride and bromide, as well as with the haloid salts of thallium,[49] it must be concluded that all these sub-

[45] "Die neue Welt der flüssigen Kristalle," 1911. [46] "Flüssige Kristalle," 1904.

[47] O. Lehmann, *Zeitsch. Kryst. Min.*, 1913, **52**, 597.

[48] C. Tubandt and E. Lorenz, *Zeitsch. physikal. Chem.*, 1914, **87**, 527; *A.*, ii, 516.

[49] H. Stoltzenberg and M. E. Huth, *ibid.*, 1910, **71**, 641; *A.*, 1910, ii, 295.

stances must be definitely deleted from the list of liquid crystals. It must here be noted that the real point at issue is not so much whether any particular "solid," crystalline substance, say, silver iodide, is so soft that it would be a misnomer to term it a solid—a decision in either sense would not be particularly momentous—but rather whether the turbid, doubly refracting liquids are restricted to organic compounds of some molecular complexity, or whether representatives are also to be found among simple binary compounds. This is, indeed, a question of some theoretical importance.

Enough has been said to indicate that the use of the term liquid crystal was quite premature from the outset. Some recent work on the geometrical form of ammonium oleate and *p*-azoxybenzoic ester has led the authors [50] to the conclusion that the shapes have no similarity whatever with crystal forms, but are figures of revolution of extraordinary complexity. Again, with regard to the optical properties of the more mobile substances,[51] which, of course, cannot be said to have any shape, it has been found that there is a continuous internal movement even in the smallest discrete globule that can be isolated for purposes of observation. The movement increases in intensity as the temperature is raised, and does not appear to have any definitely regular character. The composite nature of such globules was, of course, recognised by Lehmann, who has frequently been compelled to point out that a globule is not a liquid crystal, but an aggregate of liquid crystals. It will be realised how impossible it is to substantiate the crystal character of such unpromising material.

Homogeneous masses of material, suitable in every way for experiments of some precision, first became available as a result of Vorländer's [52] numerous syntheses of complex aromatic derivatives, which, when melted on a glass slide, with or without a cover slip, yield a clear mass of doubly refracting liquid. When viewed in convergent light there results in every case a normal uniaxial interference figure with an extraordinarily perfect definition; moreover, if the substance has an enantiomorphous molecular configuration, the interference figure shows rotatory polarisation. In thicknesses greater than 0·3 mm. the masses tend to be slightly turbid. The values of the two indices of refraction ϵ and ω have been determined with great accuracy.[53] The fact that the existence of biaxial liquid crystals has never been established whilst some fifty compounds are definitely known to be uniaxial,[54] is of superlative importance, inasmuch as it presents a statistical proof that the structure is not crystalline (the proof is really very strong, since nearly all chemical substances, having a complex chemical structure, crystallise in biaxial systems). The whole of the firmly established properties, dichroism and the invariable straight extinction when the "crystal" is resting on a "prism" face, the apparent absence of double refraction in parallel light, and the perfect uniaxial figure in convergent light, when the "crystal" is resting on its "base," are in complete harmony with a structure analogous to that of an even-grained piece of wood. These considerations led Bose to advance the "swarm theory," which has dominated the work of the last few years.

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[50] G. Friedel and F. Grandjean, *Bull. Soc. franç. Min.*, 1910, **33**, 192, 409, 466; *A.*, 1910, ii, 809, 1018.

[51] C. Mauguin, *Compt. rend.*, 1912, **154**, 1359; *A.*, 1912, ii, 630.

[52] D. Vorländer, *Ber.*, 1908, **41**, 2033; *A.*, 1908, i, 641. "Kristallinischflüssige Substanzen," 1908.

[53] *Ann. Report*, 1910, 11.

Bose's Swarm Theory.[55]

In all theoretical discussions of the molecular theory of liquids it is presupposed for purposes of simplicity that the molecule is spherical. This supposition can, of course, only be true for liquefied monatomic elements; it can scarcely hold for a molecule like anisaldazine, $MeO\cdot C_6H_4\cdot CH\colon N\cdot N\colon CH\cdot C_6H_4\cdot OMe$. If two or more elongated molecules approach each other so closely that the mean distances of their centres of gravity are less than half the length of the molecule, all free rotation must cease except about the direction of elongation, and a stable tendency towards a parallel arrangement may set in. Now a large bundle or swarm of parallel molecules in a perfectly fluid condition and without any suspicion of a space-lattice arrangement will evidently possess the symmetry of a figure of rotation, and optically should behave as a uniaxial crystal. Each swarm or homogeneous tract ("liquid crystal") will be quite clear and transparent, the turbidity of a large mass of liquid being simply due to the reflection and diffusion of light at the mutual boundaries of the swarms. The average size of the swarm decreases on heating; the point at which the swarms become smaller than the wave-length of light is the clearing point. Above this temperature the liquid is to all intents and purposes singly refracting. A rough idea of the structures of isotropic and anisotropic liquids will be gained from Fig. 9, in which *a* is meant to illustrate the state of affairs in the ordinary isotropic liquid, which on cooling passes into the swarms of parallel molecules shown in *b*; the optical behaviour of a single swarm, as exemplified by Vorländer's viscous substance, is shown at *c*.

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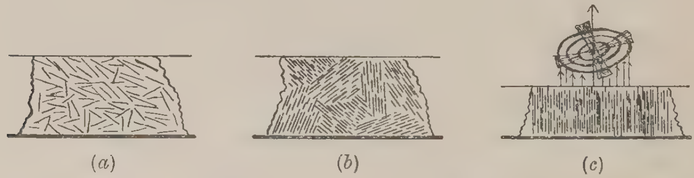
[54] D. Vorländer, *Physikal. Zeitsch.*, 1914, **15**, 141.

[55] E. Bose, *ibid.*, 1907, **8**, 347, 513; *A.*, 1907, ii, 443; *ibid.*, 1908, **9**, 708; *A.*, 1908, ii, 1017.

General Evidence in Support of the Theory.—The theory is in good accord with all the general physico-chemical properties. To begin with, the change, crystal ⟶ anisotropic liquid, is not only quite sharp, but is also accompanied by a considerable absorption of heat (about 20 calories). On the other hand, the change, anisotropic liquid ⟶ isotropic liquid, is not only characterised by a low heat absorption (about 1 calorie), but also appears to be a gradual process extending over one or two degrees of temperature.* This important fact has been brought out by Bose's viscometric work.[56] In the case of anisaldazine the viscosity of the isotropic liquid increases quite normally with the fall of temperature to the point of turbidity, and then decreases very sharply to a minimum at 2° below the clearing or turbidity point. The viscosity then begins to suffer the normal increase with fall of temperature, but it does not succeed in attaining anything like the value enjoyed by the isotropic liquid. The lower value of the viscosity of the anisotropic liquid, as compared with the isotropic liquid, constitutes the so-called "viscosity anomaly." Its interpretation was given by Bose[57] on a kinetic basis. If the form of the molecule be taken to be that of an elongated ellipsoid of rotation, the viscosity of a swarm can theoretically sink to two-thirds the value of the viscosity of the same substance in the isotropic condition; further, the supposition of a three axial ellipsoid could account for even lower values. The ratio of the viscosities, anisotropic : isotropic is 0·65 for anisaldazine. It has also been found that the change, isotropic ⟶ anisotropic is always accompanied by a moderate increase of density, as might be expected from the closer packing that is obviously compatible with the parallel arrangement of elongated molecules.

Fig. 9.



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* The crystalline nature of anisotropic liquids was accepted by Roozeboom, who accordingly regarded the clearing point as the true melting point, the point at which the solid crystal melts to give the anisotropic liquid being regarded as a polymorphous transition point. This decision must now be reversed; at any rate, it is more consequent to regard Roozeboom's "transition point" as the true melting point.

[56] E. Bose and F. Conrat, *Physikal. Zeitsch.*, 1908, **9**, 169; *A.*, 1908, ii, 258.

[57] E. Bose, *ibid.*, 1909, **10**, 230; *A.*, 1909, ii, 383.

Magneto-optical Researches.—The investigation of the optical behaviour of anisotropic liquids under the influence of an electromagnetic field has attracted the attention of several workers, and the results are regarded by some, including Nernst,[58] as affording a decisive proof of the correctness of the swarm theory.

It was early observed by Lehmann that a magnetic field has a clearing effect on droplets of *p*-azoxyanisole. Bose[59] investigated the effect on relatively large masses of liquid; with anisaldazine the effect begins with the application of 600 Gauss units of force, and, by means of a few thousand units, layers up to 4 mm. are immediately cleared when the direction of vision is along the lines of force. On turning off the current, the mass immediately becomes turbid. Similar results were obtained with *p*-azoxy-anisole and -phenetole.

The work was carried a step forward by Mauguin,[60] who showed that the very mobile *p*-azoxyphenetole may be obtained in clear masses provided that both slide and cover slip are thoroughly cleansed with hot sulphuric acid, distilled water, and ether; such a preparation gives a normal uniaxial figure. The same substance was then investigated under the action of a magnetic field, and the following three fundamentally important observations were made: (1) layers up to 2 mm. may be rendered quite clear and transparent, no matter whether viewed along or across the lines of force; (2) when examined between crossed nicols, the behaviour is in every respect analogous to that of a uniaxial crystal—uniform darkness when viewed along the lines of force in parallel light and a perfect uniaxial figure in convergent light; normal extinction in four positions when viewed across the lines of force. The double refraction is strong, and increases up to the application of 5000 Gauss units, and then remains constant up to 7000; (3) when a homogeneous film between slide and cover slip, as in Fig. 9*c*, is subjected to the action of a transverse magnetic field, the optic axis is gradually deflected away in the plane containing the lines of force. On releasing the force, the optic axis immediately returns to the normal position. Similar results, although not quite so complete, were independently obtained by Wartenberg[61] for both *p*-azoxyanisole and -phenetole; the double refraction of the latter was found to be by far the stronger.

T. V. Barker.

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[58] W. Nernst, *Zeitsch. Elektrochem.*, 1910, **16**, 702.

[59] E. Bose, *Physikal. Zeitsch.*, 1911, **12**, 60; *A.*, 1911, ii, 184.

[60] C. Mauguin, *Compt. rend.*, 1911, **152**, 1680. See also ref. 51.

[61] H. v. Wartenberg, *Physikal. Zeitsch.*, 1911, **12** 837, 1230; *A.*, 1911, ii, 952; 1912, ii, 112.

RADIOACTIVITY.

The Atomic Weight of Lead.

The theoretical prediction that the atomic weight of lead from radioactive minerals should differ from 207·1, the international figure, that from uranium minerals tending towards the number 206, and that from thorium minerals towards the number 208,[1] has now been examined experimentally by several observers. The results obtained, although in all cases as yet of a preliminary character only, show clearly that the atomic weight of lead from radioactive minerals differs from the international value and varies with the character of the mineral from which the lead is derived.

In the first results to be published, the mineral examined was Ceylon thorite,[2] which is uniquely suitable for the investigation of the question, as regards thorium, since the ratio of uranium to thorium is exceptionally low, and the amount of lead is so small that it may well be all of radioactive origin. The thorium content is about 55 per cent., the uranium content between 1 and 2 per cent., and the lead about 0·4 per cent.

If the law of the conservation of mass held during radioactive changes, and the rigid correctness of this assumption is now open to doubt (p. 271), if all the lead in the mineral were of radioactive origin, and if the lead derived both from the thorium and the uranium were entirely stable and accumulated linearly with the lapse of time, it is to be expected that the atomic weight of the lead from Ceylon thorite should be rather more than one unit higher than the international figure. The rate of change of uranium is probably between 3 and 2·5 times that of thorium, so that, on the above assumption, the lead should be derived at least ten parts from thorium to each part from uranium. The calculated atomic weight of the former is 208·4, and of the latter 206·0, since they are derived from thorium, 232·4, and radium, 226·0, respectively, by the loss of six and five atoms of helium. The calculated atomic weight of the thorite lead should therefore be about 208·2.

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[1] *Ann. Report*, 1913, 269.

[2] F. Soddy and H. Hyman, *T.*, 1914, **105**, 1402. This paper was read on May 7th, 1914, and an abstract appeared in the *Morning Post* on the following day, and in the *Proceedings* on May 18th, 1914.

In the experimental work, a kilogram of the mineral was worked up, and only 1·2 grams of purified lead chloride were finally available. It was purified chiefly by precipitation as sulphate and as sulphide and by crystallisation as iodide, and its atomic weight was estimated purely relatively against that of ordinary lead (purified in an identical series of operations), volumetrically by titration with the same silver nitrate solution. The lead chloride was finally weighed in a platinum boat, after fusion in hydrogen chloride and cooling in nitrogen, as recommended by Baxter and Wilson. The mean of two determinations showed a difference of 1 part in 225 in the volume of silver solution required for equal weights of the two lead chlorides, which is certainly many times greater than the possible error of the experiment unless unknown sources of error existed. The atomic weight of the thorite lead, calculated from that of ordinary lead as 207·1, was 208·4.

Photographs of the spectra of the two specimens of lead, taken by the Féry spectrograph, showed complete identity, both in the wave-lengths and the relative intensity of the lead lines, with the single exception of one line, 4760·1, which was much stronger in the photographs of ordinary lead than in those of the thorite lead. As the whole series of experiments are now being repeated *de novo* with the lead derived from 30 kilograms of hand-sorted thorite, discussion of these results may be deferred.

In the next results published,[3] the atomic weight of lead from five radioactive minerals, uraninite (N. Carolina), pitchblende (Joachimsthal), carnotite (Colorado), thorianite (Ceylon), and pitchblende (Cornwall), and from two commercial products, not radioactive, was determined by the accurate methods developed in the Harvard laboratories, and used by Baxter and Wilson in their previous determination of the atomic weight of lead. The lead from N. Carolina, uraninite, was a small sample of 3·8 grams of chloride, separated from 110 grams of the purest selected mineral by Boltwood and Gleditsch; that from Joachimsthal pitchblende and Colorado carnotite had been separated by Fajans; that from Ceylon thorianite was part of 1100 grams of nitrate separated by Boltwood from 25 kilograms of mineral; and that from Cornish pitchblende was from residues supplied by Sir William Ramsay. The methods of purification used were chiefly the recrystallisation of the nitrate and the chloride, and the precipitation of the dilute solution of the latter by hydrogen chloride. The final values obtained are shown below:

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[3] T. W. Richards and Max E. Lembert, *J. Amer. Chem. Soc.*, 1914, **36**, 1329; *Compt. rend.*, 1914, **159**, 248; *A.*, ii, 653. These results were not published by the authors until after the researches about to be considered, but a preliminary announcement of them was made by K. Fajans under the title "Nachtrag zu dem Aufsatz 'Die Radioelemente' und das periodische system,'" *Naturwissenschaften*, May 29th 1914; also later in *Sitzungsber. der Heidelbergen Akad. der Wiss.*, 1914, Abt. *A.*, Abh. 11.

Lead from N. Carolina uraninite	206·40
,, ,, Joachimsthal pitchblende	206·57
,, ,, Colorado carnotite	206·59
,, ,, Ceylon thorianite	206·82
,, ,, Cornish pitchblende	206·86
Common lead	207·15

In the next series,[4] the lead from three uranium minerals containing negligible quantities of thorium, pitchblende, carnotite, and yttro-tantalite, from one thorium mineral containing very little uranium, monazite, and from ordinary galena, was examined. It was separated as metal from the crude carbonates by fusion with cyanide, converted into the nitrate and precipitated as sulphate, converted into carbonate and again precipitated as sulphate, separated as oxide by electrolysis, reduced to metal by cyanide and converted into nitrate, and then into basic nitrate by heat. The basic nitrate, dissolved in water, was filtered from the insoluble fraction, converted into nitrate, crystallised, and finally obtained as metal. The method of estimation of the atomic weight was to weigh the metallic lead in a quartz vessel, to dissolve it in concentrated nitric acid, and to dry to constant weight at 145° to 150°, weighing it again as lead nitrate. This is one of the methods employed by Stas, and for relative estimations has advantages over the more accurate silver method in requiring less manipulation of the substance. The lead was purified in each case by a series of operations until it showed the same atomic weight after a fresh purification. The values found are shown below:

Lead from carnotite	206·36
,, ,, yttro-tantalite	206·54
,, ,, pitchblende	206·64
,, ,, monazite	207·08
,, ,, galena	207·01

Unfortunately, the sources of the radioactive minerals are not given.

Lastly,[5] the atomic weight of the lead from Joachimsthal pitchblende was accurately determined by Baxter's method. It was purified chiefly by crystallisation of the nitrate from the hot solution by the addition of nitric acid, followed by solution of the chloride in saturated hydrogen chloride solution and precipitation with water. The value 206·736 was obtained as the mean of six determinations varying over the extremes of 0·03 unit, and of three determinations varying over 0·018 unit. The possibility is mentioned that, by selecting the pitchblende from isolated pieces of blende, a lead might be obtained of still lower atomic weight.

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[4] Maurice Curie, *Compt. rend.*, 1914, **158**, 1676; *A.*, ii, 563.

[5] O. Hönigschmid and Mlle. S. Horovitz, *ibid.*, 1796; *A.*, ii, 653.

Bearing in mind that two out of the four researches detailed have been carried out by chemists experienced in atomic-weight determinations, and that much of the mineral examined was no doubt of very mixed composition, so that not all the lead present can be reasonably assumed to have been of radioactive origin, it is clear that the theoretical predictions have received remarkable confirmation from this first preliminary experimental examination. Further results with carefully selected minerals must be awaited. That an investigator as experienced in atomic-weight work as Professor T. W. Richards should regard his results as definitely establishing a variation in the chemical equivalent of lead from different sources, whereas earlier experimental investigations at Harvard on this very question, in the case of the elements copper, calcium, sodium, and iron, all gave completely negative results, is perhaps the chief result gained.

The lowest value recorded, 206·40, is for carefully selected uraninite, and the highest, 208·4, is for thorite containing a nearly negligible proportion of uranium. The two values, 206·57 and 206·74, obtained by equally skilled workers for Joachimsthal pitchblende, clearly indicate variations in the character of the material worked on, and the same explanation may possibly cover the variations found for the other thorium-free uranium minerals, but the values for the thorium minerals, Ceylon thorianite, 206·82, and monazite, 207·08, are lower than would be anticipated if the end-product of thorium is stable and has the calculated atomic weight 208·4, although it must be remembered that, owing to its greater rate of change, the uranium would be some three times as efficient a lead producer as the thorium. In neither case are the essential data given as to the ratio of uranium to thorium in the minerals. For an average thorianite, this ratio would be, perhaps, 1 to 4 or 5, and for an average monazite, perhaps 1 to 8 or 10, so that in each case a value well above 207 might be anticipated.

The Stability of Lead from Thorium.

Independently of direct experimental data, the instability of the end-product of thorium, the isotope of lead with a calculated atomic weight 208·4, has been presumed. Boltwood, and later Holmes, have concluded from the lead content of uranium and thorium minerals that lead could not be the end-product of thorium, but in the original conclusion old analyses of the minerals, made before the real significance of the lead content was appreciated, seem to have been too much trusted. Thus it may be mentioned that for Ceylon thorite itself, actually containing 0·3 to 0·4 per cent. of lead, which corresponds with more than 100 million years' production, a blank appears under the column "PbO" in the original careful analysis made ten years ago. The thorium minerals are certainly less rich in lead than the uranium minerals, but then the rate of change of uranium is three times greater than that of thorium.

From an old analysis of a Norwegian thorite, returned as containing 46 per cent. of thorium, 0·4 per cent. of uranium and less than 0·1 per cent. of lead, it has been calculated[6] that the upper limit of the half-period of thorium lead cannot exceed 2×10^7 years, whilst from another analysis, in which 0·02 per cent. of lead was stated to be present, a figure ten times smaller is indicated. These calculations, however, assume the equilibrium between the thorium and lead has been reached, and, in the absence of information as to the age and character of the mineral, may possess little reality, either on the experimental or theoretical side. The same may be said of the application of the supposed connexion between the stability of isotopes and their atomic weights,[7] which at best is but partly true, and can only indicate the result that "thorium" lead is likely to be less stable than "uranium" lead if it is assumed, not only that "thorium" lead does in fact disintegrate, which is the question being discussed, but also that it disintegrates, giving β- rather than α-rays.

A recent examination of the lead–thorium and lead–uranium ratio of a series of minerals from the Langesund-fjord district, south of Christiania, Norway, all of Devonian age and "almost certainly "Middle Devonian,"[8] for which, from the lead-uranium ratio, the mean value of the age of the formation had been previously deduced as 370 million years,[9] gives some indirect information on the question whether the end-product of thorium is lead. The ratio of thorium to uranium varied in the different minerals over a range of 180. The lead–uranium ratio was, on the whole, remarkably constant, but there was no constancy whatever in the lead–thorium ratios. The ratio calculated on the assumption that lead was the product both of thorium and uranium was less constant on the whole than the lead–uranium ratio. Two thorites, however, were notable exceptions, the lead–uranium ratio being between two and three times as high as the mean for the others. It may be mentioned that for the majority of the minerals examined the actual lead content was below 0·01 per cent., and the calculations naturally depended entirely, in the case of these minerals, on the possibility of determining such minute quantities with accuracy. Other series of minerals of less definite geological age are cited in support of the view that the thorium end-product is not lead.

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[6] K. Fajans, *Sitzungsber. Heidelberger Akad. Wiss.*, 1914, Abt. *A.*, Abh. 11.

[7] *Ann. Report*, 1913, 269.

[8] A. Holmes and R. W. Lawson, *Phil. Mag.*, 1914, [vi], **28**, 823; *A.*, 1915, ii, 5.

[9] *Ann. Report*, 1911, 295.

It is difficult at the present stage to evaluate the precise bearing of this evidence. Admittedly it shows—the point, indeed, was not in doubt—that some of the lead is derived from the uranium, and therefore no constancy is to be anticipated in the lead–thorium ratio; but the further point that none is derived from the thorium involves, perhaps, greater trust in the method and in the analyses than is justifiable. The relatively slow rate of change of thorium, the dubiety regarding the age and unaltered character of the mineral, the lack of information regarding the initial lead content in the mineral, and the exceptions referred to, must all be taken into account, and it may well be doubted whether what is really rather a fine point can be settled by such means. The conclusions appear to be biassed also by the doubtful theoretical deduction that, since the uranium isotope of lead is stable, the uranium and thorium isotopes cannot both be stable, and therefore the thorium isotope is unstable. Against such reasoning, that because one isotope is stable another of different atomic weight cannot be stable, the fact of the difference between the atomic weights of common lead and of lead of radioactive origin may now be cited. The question is still *sub judice* until further atomic-weight estimations are available.

The Conservation of Mass in Radioactive Change.

The recent determinations of Hönigschmid on the atomic weight of radium, for which he obtained the value 226·0, lead to a calculated value for the atomic weight of uranium of practically 238·0, if mass is conserved in radioactive changes, instead of 238·5, the international number. A revision of the atomic weight of uranium has now been carried out[10] by the method of Richards and Merigold, except that quartz vessels were employed instead of vessels of porcelain and glass, which are slowly attacked both by the bromine and the uranous bromide used. The first series of experiments with uranous bromide, distilled, melted, and solidified in bromine vapour, in which the ratios $UBr_4 : Ag$ and $UBr_4 : AgBr$

[10] O. Hönigschmid, *Compt. rend.*, 1914, **158**, 2004; *A.*, ii, 654.

were determined, gave as the mean of eight experiments the value 238·08. In a second series, the uranous bromide was distilled, melted, and solidified in a current of nitrogen. Fourteen experiments gave the mean value 238·175. The first series, where, perhaps, the bromine is in excess, gives a minimum value, and the second series the most probable value for the atomic weight. Although considerably nearer the whole number than the international value, it departs from it sufficiently far to leave the question open whether the mass of the atom of radium and the three α-particles expelled is exactly equal to the mass of the uranium atom from which they are derived.

In view of the fact that so many of the atomic weights approximate to whole numbers in terms of that of oxygen as 16, whilst some depart notably from whole numbers, this question is of prime importance in problems concerning the origin and genesis of the elements.

It has been suggested[11] that in the disintegration or coalescence of atoms a change of mass may occur proportionate to the change of energy, a loss of mass corresponding with a liberation of energy and a gain of mass with an absorption of energy, in each case equal to the energy which the mass lost or gained would possess, if moving with the velocity of light.

The Mass and Velocities of the α-Particle. Radium Constants.

In this connexion may be discussed a new determination of the mass and velocities of α-particles,[12] which was designed to test as thoroughly as possible whether the mass of the helium atom travelling at high speed, which constitutes the α-particle, was identical with that found for the atomic weight of helium, the older determinations having indicated a mass some 4 per cent. less. From ordinary electrochemical data, that is to say, the value of the faraday, the ratio of the charge to the mass of the hydrogen ion is 9670. With 3·998 taken as the mean of recent atomic-weight determinations for helium, the value for the "bivalent" α-particle should be 4826 instead of 5070, the experimental value. By the exercise of great care and the experience accumulated in a long acquaintance with the problem, an accuracy of 1 part in 400 was secured finally in the measurements of this ratio from the magnitude of the electromagnetic and electrostatic deviations of the α-particles from radium emanation, radium-*A*, and radium-*C* in a vacuum. Values lying between 4813 and 4826 were obtained, the mean being 4820, which agrees with the calculated value within the limits of experimental error.

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[11] Sir J. J. Thomson, "The Atomic Theory," Romanes Lecture, 1914, p. 16.

[12] Sir E. Rutherford and H. Robinson, *Phil. Mag.*, 1914, [vi], **28**, 552 ; *A.*, ii, 789.

The new value for the initial velocity of the α-particle of radium-*C*, namely, $1{\cdot}922 \times 10^9$ cm. per second, is some 7 per cent. smaller than the previous one. Before, the experimental value for the development of heat from radium agreed excellently with that calculated from the thermal equivalent of the kinetic energy of the α-particles expelled. On the new data, however, the observed heat effect is some 7 per cent. greater than that calculated from the mass and velocities of the expelled α-particles, including, of course, the kinetic energy of the recoil atoms. It is by no means necessary that the total heat energy of radioactive change should be the same as the kinetic energy of the products. It may be either greater or less, according as the change itself is exothermic or endothermic. In other words, the kinetic energy of the α-particles and of the recoil atoms will together equal the heat evolution only if they are entirely responsible for the thermal effect. Rutherford[13] suggests that in an α-ray change, wherein the magnitude of the nuclear charge of the atom decreases, there is a decrease in the energy of the electronic system around the nucleus, which presumably appears as heat, and calculates that some 10 per cent. of the thermal evolution is due to this cause, only 90 per cent. being due to the mechanical energy of the expelled α-particle. In a β-ray change, on the other hand, wherein the nuclear charge increases, a corresponding increase of the internal energy of the electronic system of the atom occurs. This is supported by the fact that the heat evolution of radium-*B* and -*C* together, in which β- as well as α-rays result, is less than is to be expected from the evolution of the emanation and of radium-*A*, in the change of which α-rays only are expelled. The view, on close examination, seems to present some difficulties of a fundamental character, not so much during an α-disintegration where the residual atom may evolve other energy which afterwards appears as heat, as during a β-ray disintegration, where a transformation of heat of the surroundings into internal atomic energy seems to be required.

In the same paper Rutherford revises all the radium constants given in his "Radioactive Substances and their Radiations" in terms of the International Radium Standard. The half-period of radium is 1690 years, or average-life period 2440 years, calculated by taking the number of α-particles expelled per gram of radium (by itself) per second as $3{\cdot}57 \times 10^{10}$ and $4{\cdot}61 \times 10^{-10}$ E.S.U. as the value of the atomic charge. The experimental values for the half-period, 2000 years (Boltwood), 1800 years (Keetman), and 1730 years

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[13] Sir E. Rutherford, *Phil. Mag.*, 1914, [vi], **28**, 320 ; *A.*, ii, 788.

(Stefan Meyer) are considerably higher than the calculated value, but the latter depends upon the agreement of so many independent data that it is unlikely to be seriously in error. The Boltwood-Rutherford uranium ratio of radium to uranium in minerals on the international standard is $3 \cdot 23 \times 10^{-7}$, but a more accurate determination of this important constant is much to be desired.

α-Particles and "H-*Particles.*"

Rutherford's nuclear theory of atomic structure leads to some interesting consequences when collision occurs between the α-particle and an atom of similar or smaller mass, and the effect on the collision on the atom struck, as well as on the velocity of the α-particle, is important.[14] In the case of helium, where the masses of both atoms are alike, the result follows that no encounter can deflect the α-particle from its course through an angle greater than a right angle, whereas in the case of hydrogen the angle of maximum deflexion is 14°29′. In the latter case, an undeflected α-particle may signify one that has not been in collision at all, or one that has experienced a perfectly full collision and followed on in its initial path behind the more rapidly recoiling hydrogen atom. On certain assumptions, it was estimated that the maximum velocity which a recoiling hydrogen atom could thus acquire was 1·6 times that of the α-particle striking it, and its "range" in hydrogen should be 117 cm., or possibly more.

In an experimental search for such recoiling hydrogen atoms, or "H-particles,"[15] in which a movable source of α-particles was placed in a wide tube filled with hydrogen at variable pressure, scintillations, few in number and less intense than those produced by α-particles, were observed on a zinc sulphide screen, placed at the end of the tube, far beyond the extreme range of the α-particles themselves in hydrogen. In air, no such scintillations were observed. In hydrogen, a suitable aluminium screen, placed directly in front of the source of α-particles, suppressed these scintillations, but when placed near the screen the scintillations were again seen, showing that they have their origin in the hydrogen, by impact of the α-particles. So far as could be seen, these "H-particles" obey a similar law of absorption in various metal foils to that obeyed by the α-particles, but it is to be expected that they will prove much more penetrating, on account of their greater velocity and smaller mass.

A special search for radiant particles, differing either in mass or charge from the α-particle, in the disintegration of radium emanation gave completely negative results.[16]

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[14] C. G. Darwin, *Phil. Mag.*, 1914, [vi], **27**, 499; *A.*, ii, 324; Sir E. Rutherford, *ibid.*, 488; *A.*, ii, 323.

[15] E. Marsden, *ibid.*, 824; *A.*, ii, 407.

γ-*Rays.*

Foremost in interest in connexion with the physics of radiations has been the determination of the wave-lengths in the spectra of the γ-rays by reflection from crystal surfaces, the first step of which was announced last year.[17] First, however, may be mentioned the completion of the researches on the analysis of γ-rays by means of their absorption-coefficients, by the examination of the uranium γ-rays.[18] These rays come from uranium-X_1 and -X_2, but their origin, as between these successive products, is undecided, although by analogy it may be surmised that only the most penetrating type comes from uranium-X_2. Three types were distinguished. For the first, which comprises 40 per cent. of the total, the value of μ/d in aluminium is 8·9, for the second 0·26, and for the third 0·052. The first is probably a characteristic X-radiation of the L-series. The value of the atomic weight of uranium-X, 234, and the value of μ/d, 8·9, compared with these values for mesothorium-II, 228 and 9·5 respectively, favour the view that radioactinium, with μ/d intermediate at 9·2, has an intermediate atomic weight, 230, and therefore that actinium also has the atomic weight 230, which is a point of considerable importance.[19] However, this would make the atomic weights of actinium-B and radium-B identical, whereas the values for μ/d of their characteristic X-radiations are, respectively, 11·4 and 14·7. Hence the evidence from this source is conflicting.

The examination of the γ-rays from radium-B and -C by reflection from crystal surfaces,[20] in addition to its intrinsic interest, has also been the means of putting to an unexpected experimental test the prediction from the theory of isotopes, that the spectra of isotopic elements would prove identical.[21] The main lines in the spectrum of the soft γ-rays of radium-B are reflected from rock-salt at angles almost exactly 10° and 12°, and the wave-lengths calculated from them, in Angström units (10^{-8} cm.), are 0·982 and 1·278 respectively. By extrapolation from Moseley's results (p. 277) for the wave-length of the L-series characteristic X-ray of gold to that of lead, it was calculated that the characteristic

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[16] Sir E. Rutherford and H. Robinson, *Phil. Mag.*, 1914, [vi], **28**, 552; *A.*, ii, 789.

[17] *Ann. Report*, 1913, 283.

[18] H. Richardson, *Phil. Mag.*, 1914, [vi], **27**, 252; *A.*, ii, 160.

[19] Compare *Ann. Report*, 1913, 269.

[20] Sir E. Rutherford and E. N. da C. Andrade, *Phil. Mag.*, 1914, [vi], **27**, 854; **28**, 263; *A.*, ii, 408, 698.

[21] See *Ann. Report*, 1912, 322, for the original suggestion.

X-ray of lead should be reflected from a rock-salt crystal at an angle of 12·07°, whereas the strongest line in the radium-*B* γ-ray spectrum is reflected at 12·05°. Fleck has shown that radium-*B* is isotopic with lead, and, in order to test directly whether the characteristic *X*-ray spectrum of lead would prove identical with the γ-ray spectrum of radium-*B*, the latter was compared directly with that of the secondary γ-rays generated in a block of lead by impact of β-rays. Only faint lines were obtained in the latter case, but two of them gave reflection angles of 10°2′ and 12°0′, in good agreement with the radium-*B* lines. On substituting for the block of lead one of platinum, quite distinct lines resulted. The atomic weight calculated for radium-*B* is 214, whereas that of lead is 207, and the authors conclude that the hypothesis that isotopic elements of different atomic weights have identical spectra is verified in an unexpected manner.

In the further examination of the more penetrating γ-rays of radium-*B* and -*C*, new methods of greater accuracy were developed, in which the rays were transmitted through a crystal and fell normally on a photographic plate. Blank absorption lines and enhanced reflected lines on the plate both gave the angles of reflection required with considerable accuracy. The spectrum of radium-*C* γ-rays appears to consist of lines reflected from rock-salt at angles 44′, 1°0′, 1°11′, and 1°24′, with wave-lengths of 0·071, 0·099, 0·115, and 0·137 in Ångström units. For radium-*B*, the spectrum of the penetrating γ-rays appears to consist of lines reflected at 1°37′, 1°44′, 2°0′, 2°20′, 2°28′, 2°40′, 3°0′, 3°18′, 4°0′, 4°22′, with wave-lengths 0·159, 0·169, 0·196, 0·229, 0·242, 0·262, 0·296, 0·324, 0·393, and 0·428, of which, possibly, the third and second from the last are second-order repetitions. The most important are the lines reflected at 1°, and the close doublet reflected at 1°37′ and 1°43′. In a later paper[22] this is regarded as probably having one component due to radium-*B* and one to radium-*C* (see p. 283).

The shortest wave-length, 0·071, that of one of the radium-*C* γ-rays, is seven times shorter than the shortest hitherto measured, namely, the *K*-series *X*-ray line of silver, and the authors express surprise that the architecture of the crystal is fine and definite enough to resolve it. Although the range of the thermal agitation of the atoms in the crystal might be expected to be of the same order of length, yet placing the crystal in liquid air did not improve its resolving power.

It is probable that one of the lines of wave-length 0·159 and 0·169 is a characteristic *X*-ray line of the *K*-series of lead (radium-*B*), but the lines of radium-*C* cannot belong to the *K*-

[22] Sir E. Rutherford, *Phil. Mag.*, 1914, [vi], **28**, 305; *A.*, ii, 789.

series of bismuth, and are probably in a new and hitherto unobserved series of higher frequency, which is named the *H*-series.

The work on γ-rays, although as yet not complete, raises the expectation that the complicated mixtures of γ-radiations given by the radio-elements will all be resolved into characteristic *X*-rays of one or other of three series, the *L*, *K*, and *H* series, the wavelengths and penetrating powers of the three series being simply related to one another on the one hand, and on the other to the atomic number of the source, the greater the atomic number, or the nearer the element is to the end of the Periodic Table, the shorter being the wave-length and the higher the penetrating power.

The difficult question of the hardening of γ-rays of radium-*C*, whereby, by passage through a heavy metal, the rays become more penetrating to a lighter metal, has been recently re-examined.[23] The fact that the spectrum of the γ-rays of radium-*C* comprises three lines is interesting in view of the practically exponential character of the absorption, and it is suggested that "hardening" may be due to the weeding out of the two less penetrating rays.

Of great general interest in connexion with these advances in our knowledge of γ-rays is the light thrown on the practical problem of how to generate *X*-rays as penetrating as the γ-rays of radium, and so to avoid the use of that extremely expensive substance in medicine.[24] Rutherford and Andrade deduce from Planck's relation between energy and frequency (p. 281) that with a fall of potential of 180,000 volts, which is sufficient to give a velocity 0·7 of that of light to the electron, it should be possible to generate *X*-rays as penetrating as the γ-rays of radium-*C*. With a Coolidge tube, this should not now be beyond the range of possible experimental accomplishment. This opinion is probably the reverse of what a physicist a year ago might have been inclined to give, and is very significant.

X-*Ray Spectra of the Elements.*

Last year, Moseley determined the wave-lengths of the characteristic *X*-rays of the ten consecutive elements in the Periodic Table from calcium to zinc, and found that the spectrum of each consisted of two rays, the wave-length of the stronger rays being simply connected with a set of consecutive integral numbers from 19 to 29, numbers, in fact, which represent the position of the element in the Periodic Table, excluding hydrogen, calcium being the 20th and zinc the 30th element in order of ascending atomic weight.[25]

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[23] S. Oba, *Phil. Mag.*, 1914, [vi], **27**, 601; *A.*, ii, 409.

[24] Compare also F. Dessauer, *Physikal. Zeitsch.*, 1914, **15**, 739; *A*., ii, 699.

The facts that, in radioactive changes, when two positive charges are expelled from the atom as an α-ray, the element changes its place in the Periodic Table by two places in the direction of diminishing atomic mass, and, when one negative charge is expelled as a β-ray, the element changes one place in the opposite direction, and, moreover, that all the elements occupying the same place in the Periodic Table are chemically identical, had already suggested that the successive places in the Periodic Table correspond with unit differences in the net value of the internal charge of the atom. Moseley's work gives us the means of establishing, for the first time, the relative value of this charge for each element, and the absolute number of places in the Periodic Table, over the range studied.

Since then, what amounts to a veritable roll-call of the elements has been made by this method.[26] Thirty-nine elements, with atomic weights between those of aluminium and gold, have been examined in this way, and in every case the lines of the *X*-ray spectrum have been found to be simply connected with the integer that represents the place assigned to it by chemists in the Periodic Table. That is to say, giving the atomic number 13 to aluminium, the 13th element in order of atomic weight, the atomic numbers of all the elements up to gold, the heaviest element yet examined, can be found. The atomic number thus found for gold is 79.

The general method is to plot the square root of the frequency of the ray in question against the atomic number of the element, when a series of straight lines results. For the lighter elements between aluminium and silver, the *K*-series of characteristic *X*-rays was examined, and for the heavy elements between zirconium and gold, the *L*-series. In the first case, the wave-lengths range from 8·4 to 0·56, and in the second case from 6·09 to 1·29, Ångström units. The longer waves are so easily absorbed, that the experimental difficulties are considerable, the spectrometer, as well as the *X*-ray tube, having to be exhausted. In the *K*-series two lines, and in the *L*-series five lines, exist, of which three, designated, in order of decreasing wave-length and decreasing intensity, α, β, γ, have been plotted. There is always, also, a faint companion, α', on the longer wave-length side of α, and in the rare-earth element group a rather faint ϕ-line between β and γ. In addition, there are a number of very faint lines of longer wave-length than α. When plotted as described above, each of these rays gives a separate line of slope slightly different from the others. For the *L*-series, the relation is not accurately linear, a distinct, although slight, curvature of lines being observed.

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[25] *Ann. Report*, 1913, 272.

[26] H. G. J. Moseley, *Phil. Mag.*, 1914, [vi], **27**, 703; *A.*, ii, 326.

For the α line of the K series of the light elements, the relation between frequency, ν, and atomic number, N, is given by

$$\nu = A(N-1)^2.$$

For the α line of the L-series of the heavy elements,

$$\nu = A'(N-7{\cdot}4)^2.$$

A and A' are constants connected with the fundamental Rydberg frequency, ν_0, by the relations:

$$A = (1/1^2 - 1/2^2)\nu_0 = 3/4\nu_0,$$
$$A' = (1/2^2 - 1/3^2)\nu_0 = 5/36\nu_0.$$

It will be noted that it is only for the K-series that the square roots of the frequencies of the α line are proportional to integers, which integer is one less than the atomic number or place of the element in the Periodic Table. For the L-series, the square root of the frequencies of the α line is proportional to the atomic number diminished by 7·4. In neither case is the absolute atomic number found by the generalisation, and, although for the α-line of the L series the roots of the frequencies are proportional to the numbers of the positions occupied by the elements in the Periodic Table if hydrogen is omitted, this is probably not significant.

Of greater interest to chemists will be the results as regards elements still missing and those misplaced as regards atomic weight in the Periodic Table. Thus, the elements chlorine and potassium correspond with the numbers 17 and 19, the number 18 being vacant for argon, not determined; iron, cobalt, and nickel correspond with the numbers 26, 27, 28; molybdenum, ruthenium, rhodium, palladium, silver with the numbers 42, 44, 45, 46, 47; tungsten, osmium, iridium, platinum, gold with the numbers 74, 76, 77, 78, 79. The missing numbers 43, 75, obviously correspond with the two vacancies in the Periodic Table below manganese the real existence of which the writer, at least, latterly had been inclined to doubt.

In the region of the rare-earth elements, this roll-call becomes fascinating. In this most difficult branch of experimental chemistry, how many elements have not yet been discovered, how many have aliases? Moseley finds only one place clearly vacant, namely, that between neodymium and samarium. In the following list, corrected by the author since the publication of his paper, the number in the upper column represents the atomic number, and the symbol in the lower column the corresponding element. An asterisk indicates that the atomic number has been experimentally determined from the *X*-ray spectrum. In the other cases it has been inferred:

*	*	*	*		*	*	*		*		*			
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd		Sa	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

The element tantalum, at which the normal course of the Periodic Table is resumed, has the atomic number 73, and the number 72, it is thought probable, belongs to the keltium of Urbain. Hence, counting lanthanum and cerium, but not keltium, there are fifteen rare-earth elements possible, of which fourteen are known.

There may be a re-shuffling of some of the rare-earth elements among the available places when their *X*-ray spectra have been determined, but the fact that the precise number can now be determined by this method is alone sufficient to prove its invaluableness. Again, compared with the complicated light spectra emitted by the elements, there is a simplicity and definiteness about these *X*-ray spectra which ensures that in no very long time they will supplement, if not displace, ordinary spectroscopic methods as a means of identification of elements. The difference between the two kinds of spectra, on the one hand, the light spectrum generated by the complicated electronic swarm which surrounds and hides from investigation the real material atom within, and, on the other, the *X*-ray spectrum, probably generated by a few only of the innermost electrons, is analogous to the difference between a complex cryptogram and plain writing. Perhaps not the least significant deduction which follows from this roll-call of the elements is that, on the whole, its evidence seems to be against the existence of the celestial elements coronium, asterium, nebulium, etc.

If hydrogen is the first element, gold is the 79th, and three only between these remain undiscovered, one rare-earth element and the two homologues of manganese. As the writer has shown,[27] the course of the Periodic Table from tantalum to uranium is precisely analogous to the course from vanadium to molybdenum, only two places being still vacant, namely, those of the heaviest representatives of the halogen and alkali-metal families. This gives 92 for the atomic number of uranium. Hence, from hydrogen to uranium there are 92 possible elements inclusive (not distinguishing between isotopic elements) of which five, with atomic numbers 43, 61, 75, 85, and 87, remain to be found, although the last two may be too unstable to exist.

If the periods are made to commence from the carbon family rather than from that of the inert gases, we have, before carbon, five elements belonging to the latter part of a first short period, then two complete short periods each of eight members, then two long periods each of eighteen elements, bringing the series to lanthanum. From cerium to lutecium there is the rare-earth element period of fourteen elements. Next is the missing element with atomic number 72, which may be keltium, but may be a missing analogue of zirconium, cerium, and thorium. Including it, there follows another complete normal long period of eighteen elements, and three elements of the next, before the end of the series is reached.

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[27] "Chemistry of the Radio-Elements," Part II.

The discussion of the mathematical theory of atomic structure favoured by these results, which is still in embryo, cannot be included here.[28]

Connexion between the β- and γ-Rays.

The β-rays consist of electrons moving with definite velocity, and, by the application of a magnetic field, the β-rays of many of the radio-elements can be resolved into a magnetic spectrum, consisting of a number of groups of rays having the same velocity, which are deviated to the same extent and produce definite lines, from the position of which the velocity may be deduced.[29] The γ-rays, on the other hand, have been recently proved to be light waves of excessively short wave-length, which can be determined by reflection from crystal surfaces. That a very close connexion exists between the β- and γ-rays has for long been known. Making use of Planck's relation between the frequency and the energy of radiation, Rutherford has sought, with considerable success, for a connexion between the energy of β-rays and the frequency of the γ-rays accompanying them.

It has been found[30] that when the magnetic spectrum of a source of β-rays is examined, not by the photographic method, but by Geiger's counting method, by means of the fitful discharge from a point kept at a high potential when α- or β-rays traverse the gas in the neighbourhood of the point, that the line-spectrum is of very small intensity compared with the continuous spectrum. In other words, in the case of the β-rays of radium-*B* and -*C*, for example, most of the rays are expelled with velocities uniformly distributed over a wide range, whilst the number producing the lines corresponding with groups of rays of the same velocity is relatively small. Probably the photographic plate exaggerates the relative importance of the line, as compared with the continuous spectrum.

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[28] J. W. Nicholson, *Phil. Mag.*, 1914, [vi], **27**, 541 ; **28**, 90 ; *A.*, ii, 325, 643 ; W. M. Hicks, *ibid.*, **28**, 139 ; *A.*, ii, 599 ; J. R. Rydberg, *ibid.*, **28**, 144 ; *A.*, ii, 599.

[29] *Ann. Report*, 1910, 265.

[30] J. Chadwick, *Ber. Deut. physikal. Ges.*, 1914, **16**, 383 ; *A.*, ii, 408.

Another example of the exaggeration introduced by the photographic plate is discussed under the γ-rays of radium-*B* and -*C*, in the spectrum of which the lines due to the soft rays of radium-*B* give much the most intense photographic image, although representing only 0·1 per cent. of the total γ-ray energy. Certain radio-elements like radium-*E* and uranium-*X*, the latter of which has been recently examined,[31] give few or no lines, although, in the latter case, several broad bands may be distinguished in the spectrum.

An investigation of the magnetic spectrum of the β-rays excited by the γ-rays of radium-*B* and -*C*, in various metals, by the photographic method, showed that these rays also have lines in their spectrum. When the β-rays were excited in lead, the velocities of the principal secondary β-rays were the same as those of the primary β-rays, but, when excited in gold, the velocities of the secondary rays were found to be some 2 per cent. greater than the corresponding primary rays. This is of interest, because of the isotopism of radium-*B* and lead. The primary β-rays given out by radium-*B* appear to be of identical character with the secondary β-radiation excited by γ-rays in its isotope, lead.

As a consequence of the great advances made in the last two years, Rutherford has modified his theory of the connexion between the β- and γ-rays.[32] Instead of supposing that the homogeneous groups of β-rays were due to the decrease by quanta of the energy of the primary β-particle in exciting γ-rays, it is now supposed that they arise from the collision of γ-rays with β-rays. A β-particle is expelled at a definite speed from the nucleus of the atom, and, in passing through the outer distribution of electrons, suffers collision and shares its energy with these electrons, escaping with a velocity which, as a statistical result with a large number of atoms, is continuously distributed within certain limits. Thus arises the continuous spectrum of β-rays, typical of the β-rays of radium-*E* and uranium-*X*, and important, as recent work shows, in all cases. In the next place, it is supposed that there are well-defined regions in the electronic distribution capable of being set into vibration by the passage of the β-particle, the vibrations constituting one or other of the "characteristic" γ-rays of the atoms. Accompanying the emission of these γ-rays are one or more groups of β-rays of definite speed, the latter always accompanying the former. This is in accordance with the evidence that elements like radium-*E* and uranium-*X*, which give continuous β-ray spectra, give very little γ-radiation in comparison with elements like radium-*B* and -*C*, which give well-marked β-ray line spectra and powerful γ-rays. In the γ-rays of the last-mentioned class, however, there is probably, in addition to the vibrations of definite frequency, a small part with a continuous spectrum.

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[31] O. von Baeyer, O. Hahn, and L. Meitner, *Physikal. Zeitsch.*, 1914, **15**, 649; *A.*, ii, 607.

[32] *Ann. Report*, 1912, 298; *Phil. Mag.*, 1914, [vi], **28**, 305; *A.*, ii, 789.

The above point of view requires one very interesting consequence. It is necessary to suppose that the direction of expulsion of the primary β-ray is definite with regard to the orientation of the internal atomic structure, so that whether or no γ-rays are excited depends, not so much upon whether regions capable of being set into vibration exist within the atom, as upon whether these regions are traversed by the expelled β-particle. Thus, radium-*B* and radium-*D* are isotopic, and it is to be expected that they will give identical γ-ray spectra when bombarded by β- or cathode-rays (p. 276). That their γ-ray spectra are entirely different is only intelligible if the β-particle in the two cases is expelled in different directions, traversing different vibrating regions. Using the term *X*-ray to indicate radiations generated by external bombardment of atoms by β- or cathode-rays, in contradistinction from the term γ-rays to indicate radiations generated by internal bombardment of the atom by expelled β-rays, it is to be expected that, in the former case, all possible types of characteristic radiation will have a chance of being excited, whilst in the latter case only those arising from the particular regions traversed by the definitely orientated β-ray will be generated. The energy E of a single γ-ray is regarded as emitted in quanta in conformity with what is now supposed to be true of radiation in general, and to be connected with the frequency ν of the γ-ray by the relation $E = h\nu$, where h is Planck's constant. The energies of the γ-rays in the line spectra of the penetrating γ-rays of radium-*B* and -*C* are so found. The strongest line of the radium-*C* γ-ray spectrum, that reflected from rock-salt at 1°, has an energy $1{\cdot}25 \times 10^{13}e$, where e is the atomic charge. This is very nearly three times the constant quantity of energy, $0{\cdot}4284 \times 10^{13}e$, integral multiples of which represent the energies of many consecutive lines in the β-ray spectrum of radium-*C*.[33] Another such energy quantity is $0{\cdot}74 \times 10^{13}e$, which, in multiples ranging from 2 to 23, represents the energies of some thirteen lines in the β-ray spectrum of radium-*C*. This corresponds with a γ-ray which would be reflected from rock-salt at nearly 1°40′, and is probably one of the doublet before referred to (p. 276) reflected at that angle, both of the components of which were at first ascribed to radium-*B*.

In the same way, the energies of many of the β-rays of radium-*B* agree very closely with that calculated from the frequencies of the γ-rays reflected from rock-salt at 2°20′, 2°28′, 3°18′, and possibly 1°24′. Lastly, the energies of the groups of β-rays from radium-*D* agree well with certain of the γ-rays from radium-*B*, as is a possibility in view of the isotopism of these elements. The intense soft γ-rays of radium-*B*, reflected at 10° and 12°, do not seem to be connected with any of the observed β-rays. Although giving the most intense lines, their energy is extremely small, being only some 2 per cent. of the total γ-ray energy of radium-*B*.[34] In the γ-rays of radium-*B* and -*C* together, it was estimated that the relative energies of the soft rays of radium-*B*, the hard rays of radium-*B*, and the rays of radium-*C*, are in the ratio 1 : 45 : 639 respectively.

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[33] *Ann. Report*, 1913, 280.

Electrochemical Proofs of the Theory of Isotopes.

In three different ways, the electrochemical identity of isotopic elements has been put in evidence.[35] The decomposition potential at which radium-*E* is deposited on the cathode is altered in the same direction and quantitatively to the same amount by the addition of the isotopic element, bismuth, as, according to Nernst's theory, it would be by adding the same number of radium-*E* ions, and a similar fact has been established with regard to thorium-*B* and the isotopic element, lead. Thus, in one experiment with a solution of radium-*E*, calculated to be 10^{-9} normal, a sudden increase in the quantity of radium-*E* deposited on the cathode occurred at $-0{\cdot}24V$, measured against the calomel electrode. When the normality was increased to 10^{-4} by the addition of the isotope, bismuth, the sudden increase occurred at $-0{\cdot}14V$. According to Nernst's theory, the increase of concentration ten times should change the decomposition potential $0{\cdot}018V$, so that the calculated change is $0{\cdot}09V$, and that found, $0{\cdot}10V$. With a thorium-*B* solution calculated to be $10^{-12}N$, the addition of the isotope, lead, to a normality of 10^{-3} decreased the potential at which peroxide was deposited on the anode by $0{\cdot}26V$, whereas the decrease calculated from theory is $0{\cdot}252V$.

Secondly, for the deposition of radium-*E* and of thorium-*B* at potentials below the decomposition voltage, it was shown that the addition of isotopic elements prevents this deposition, other ions being without effect. Thus, approximately 4 per cent. of the radium-*E* present was deposited on an electrode of area 1 sq. cm. in twenty-four hours, at a potential of $-0{\cdot}17V$, but when the solution was made $N/100$ with respect to bismuth ions, this deposition was prevented. Making the solution $10^{-5}N$ with respect to lead lowered the percentage of thorium-*B*, anodically deposited as peroxide, from 5 to 0·5, whilst in $10^{-3}N$-solutions no perceptible deposition occurred. The presence of thallium or of ions other than that of lead had no effect.

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[34] Miss J. Szmidt, *Phil. Mag.*, 1914, [vi], **28**, 527 ; *A.*, ii, 792.

[35] G. v. Hevesy and F. Paneth, *Physikal. Zeitsch.*, 1914, **15**, 797.

The last proof depended upon the preparation of pure radium-*D* in appreciable quantity, and its use in a galvanic chain.[36] This preparation has been previously attempted, but without complete success.[37] One curie of emanation, from the large quantity of radium available at the Vienna Institute, was sealed in a quartz vessel until its change was complete; the radium-*D* formed was dissolved in nitric acid and electrolysed. According to the conditions, the deposit could be collected as metal on the cathode or as peroxide on the anode. Preliminary experiments have shown that in the latter case 10^{-3} mg. of lead produces a clearly visible and electrochemically active deposit on a fine platinum wire. In this way, a perceptible deposit of pure radium-*D* peroxide was obtained, so free from ordinary lead that an artificial contamination by 10^{-6} mg. of lead could easily be experimentally detected. The following galvanic chain was set up,

$$\mathrm{Pt},[\mathrm{Ra}\text{-}D]\mathrm{O_2} \mid \underset{10^{-5}N}{[\mathrm{Ra}\text{-}D](\mathrm{NO_3})_2}, \underset{10^{-3}N}{\mathrm{HNO_3}}, \underset{\text{sat.}}{[\mathrm{Ra}\text{-}D]\mathrm{O_2}} \mid \underset{N}{\mathrm{KNO_3}} \mid \underset{N}{\mathrm{KCl}}, \underset{\text{sat.}}{\mathrm{Hg_2Cl_2}}, \mathrm{Hg}$$

and found to have the potential $-0{\cdot}884\,V$. By substituting for the radium-*D* peroxide electrode a similar one prepared with ordinary lead, the potential found was $-0{\cdot}888\,V$. In another research lead nitrate was added to the radium-*D* solution, and the change of potential measured for concentrations of 10^{-5}-, 10^{-3}-, and 10^{-1}-N with respect to lead, both for the lead peroxide and the radium-*D* peroxide electrode. In each case the same change of potential occurred, showing that in Nernst's equation it is the sum of the concentrations of the isotopic ions which fixes the potential of the electrode, and that lead ions and radium-*D* ions are electrochemically identical. These results probably constitute the most severe test to which the consequences of the theory of isotopic elements have as yet been put. Another investigation has shown that the electrolytic potentials of thorium-*B* and radium-*B* are the same as those of lead,[38] to an accuracy of 2×10^{-5} volt.

New Work on the Disintegration Series.

The preliminary announcement is made of the discovery of a new, long-lived member of the uranium disintegration series,[39] iso-

[36] See also *Ibid.*, *Ber.*, 1914, **47**, 2784.

[37] *Ann. Report*, 1911, 297.

[38] Z. Klemensiewicz, *Compt. rend.*, 1914, **158**, 1889; *A.*, ii, 606.

[39] K. Fajans and Helene Towara, *Naturwissenschaften*, 1914, 685.

topic with bismuth, and giving α-rays. It was thought that radium-*G*, the end-product isotopic with lead, might change with the emission of β-rays into a further product, "radium-*H*," which gave α-rays, producing an isotope of thallium. This would account for the presence of bismuth and thallium in pitchblende. The bismuth from Joachimsthal pitchblende, after purification, showed an α-activity, several times greater than that of uranium, that could not be removed by a chemical purification which would have sufficed to remove polonium, or by fractional precipitation of the oxynitrate. The range of the α-rays was found to be about 3 cm., which would correspond with a period of between 10^5 and 10^6 years. From the α-activity of the preparation, a maximum period of 10^8 years was indicated.

The origin of actinium still remains unsolved. No actinium was found in a concentrated ionium preparation four years old. An examination of pitchblende for the supposed α-ray-giving parent of actinium, the heaviest member of the tantalum family, gave no result. Tantalum, precipitated in the solution and purified, proved to be inactive. It is quite possible that "ekatantalum" departs sufficiently in chemical character from tantalum for this method to have been effective.[40]

A thorough examination of the uranium-radium ratio in carnotites of American origin led to the interesting result that when samples were taken of large lots, more than 1000 kilos., the ratio was found to be practically identical with that of pitchblende and other uranium minerals.[41] With small samples abnormal ratios, both higher and lower than the equilibrium ratios, were obtained. Apparently, local transportation of radium occurs within the ore-bed which causes differences that are completely equalised when large samples are worked upon. It is pointed out that aridity seems to be a necessary condition for the existence of carnotite beds, and that the rainfall is small. This may cause local transpositions rather than complete removal of the radium, as undoubtedly occurs with autunite.[42]

A very accurate determination of the periods of actinium and thorium emanations, in which the decay of the preparations to 1/2000th of the initial value was followed, gave the values 3·92 and 54·53 seconds respectively for the half-periods, or 5·656 and 78·69 seconds for the periods of average life.[43]

With regard to the actinium active deposit and the question whether the series branches at the *C* member, analogously to the other two series,[44] it has been reaffirmed that the α-particles, which have a range of 6·4 cm., and constitute 0·15 per cent. of the whole, are due to a branch product.[45] Confirmation of their existence has been obtained by an ionisation method, and they have been found to decay with the period of the actinium active deposit.

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[40] C. Göhring, *Physikal. Zeitsch.*, 1914, **15**, 642; *A.*, ii, 608.

[41] S. C. Lind and C. F. Whittemore, *J. Amer. Chem. Soc.*, 1914, **36**, 2066; *A.*, ii, 794.

[42] *Ann. Report*, 1909, 260.

[43] P. B. Perkins, *Phil. Mag.*, 1914, [vi], **27**, 720; *A.*, ii, 410.

A somewhat disconcerting discovery has been made with regard to the volatility of the various members of the active deposit of thorium.[46] Some evidence was obtained in 1912,[47] by L. Meitner, of a chemical separation of the two products of the active deposit, giving 35 per cent. and 65 per cent. of the α-rays respectively, by immersing nickel plates in a solution containing stannous chloride, and comparing the α-activity of the deposit with that of the solution evaporated to dryness. It appeared that the product giving 65 per cent. of the α-radiation alone was deposited, the other being left in solution. These results were criticised, and supposed to be accounted for by the abnormal volatility of the *C*-member in the presence of hydrochloric acid.[48]

In the present experiments, the active deposit was submitted to carefully regulated temperatures in an electric furnace, and the proportion of thorium-*C* volatilised was determined. From α-ray measurements, the curve of percentage volatilised, plotted against the temperature, indicated that the *C*-member was volatilised in two stages. The first stage commences at 750°, and corresponds with 35 per cent. of the α-activity, whilst the second stage begins at 900°. From β-ray measurements, however, volatilisation of the *C*-member does not appear to commence below 900°. This indicates that the *C*-member, giving first α-rays and then β-rays, is distinct from that giving first β-rays and then α-rays, instead of being the same homogeneous element disintegrating dually, in proportion 35 : 65, respectively, as has been previously assumed. Thorium-*D*, which is volatile at 500°, is known to be the product of thorium-*C* via the α, then β-change, which is the 35 per cent. branch. Additional evidence that the α-rays come from two distinct products was derived from the fact that, when heated below 900°, the β-rays from the preparation, after cooling, show an initial rise, due to re-accumulation of thorium-*D*, but above 900° no such rise occurs. Below 900°, thorium-*D*, but not its parent, is completely volatilised, whilst above 900° both parent and product are completely volatilised. The authors attempt to explain their results by supposing that the 35 per cent. of lower range α-rays, hitherto regarded as resulting in one mode of the disintegration of thorium-C, come from a new product, "C_α," of period of the order of a minute, according to the scheme:

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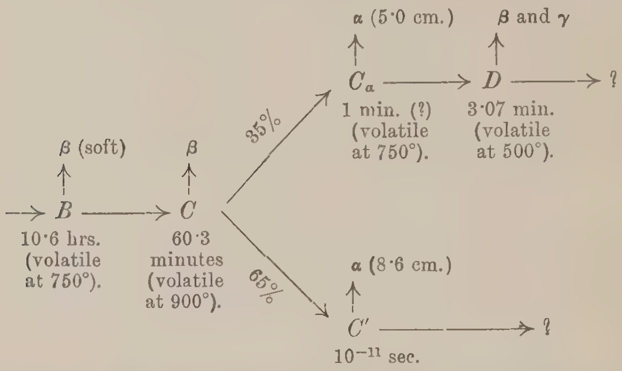
[44] *Ann. Report*, 1913, 270.

[45] E. Marsden and P. B. Perkins, *Phil. Mag.*, 1914, [vi], **27**, 690 ; *A.*, ii, 410 ; R. W. Varder and E. Marsden, *ibid.*, **28**, 818 ; *A.*, 1915, ii, 4.

[46] A. B. Wood, *Proc. Physical Soc.*, 1914, **26**, 248 ; *A.*, ii, 606.

[47] *Ann. Report*, 1912, 314.

[48] E. Marsden and R. H. Wilson, *Phil. Mag.*, 1913, [vi], **26**, 354.


α (5·0 cm.)
β and γ
C_α
D
?
1 min. (?) (volatile at 750°).
3·07 min. (volatile at 500°).
35%
β (soft)
β
B
C
10·6 hrs. (volatile at 750°).
60·3 minutes (volatile at 900°).
65%
α (8·6 cm.)
C′
?
10^{-11} sec.

It is assumed that thorium-C disintegrates dually as before, but gives β-rays, presumably, in both modes. Such an explanation appears to run counter to the periodic law generalisation, for, according to it, thorium-D should be isotopic with lead rather than with thallium. The experiments are very suggestive, and further work promised on volatilisation in atmospheres of different gases and on the behaviour of the other active deposits will be awaited with interest. In the meantime, it may be noted that there is a very direct test of the alleged separation, for a change of the 35 : 65 ratio of the long- to the short-range α-particles should occur in the above deposit, heated at temperatures between 750° and 900°. Upon the constancy of this ratio, under all conditions yet tried, the older hypothesis of dual disintegration was primarily based,[49] and it has not yet been possible to establish experimentally such a variation.

Some interesting experiments have been carried out on the volatility of thorium-D, showing that the substance, after treatment with hydrochloric acid, commences to volatilise at 270°, and is completely volatilised below 500°, whereas the untreated substance commences to volatilise at 520° and is completely volatilised at 700°. Using the volatility as a test of the state in which the thorium-D was present, the conclusions were drawn that it recoils in atomic form from the active deposit which has been treated with hydrochloric acid. On the other hand, if obtained by heating the active deposit so treated, it volatilises as chloride at the lower temperature, showing that in this case combination with chlorine must occur after its production.[50]

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[49] *Ann. Report*, 1912, 312.

Appearance of Helium and Neon in Gases Subjected to the Electric Discharge.

Numerous experiments, on the same lines as those detailed in last year's Report,[51] have been carried out on the presence of traces of helium and neon in gases subjected to the electric discharge, and the balance of the evidence appears to be against the view that these gases are transmutational products, although much, no doubt, remains to be explained concerning their apparently capricious appearances and non-appearances. Sir J. J. Thomson, whose experiments, criticised here last year, have frequently been quoted in favour of the view that the appearances are significant, himself now states: "I have never, however, been able to get any evidence, that I regard as at all conclusive, that the atom of one element could by such means be changed into an atom of a different kind; in other words, that by such means we could produce a transmutation of the elements."[52]

Merton[53] used a tap-free apparatus, essentially identical with one used by the writer in similar kind of work many years ago.[54] Hydrogen, admitted by heating, with a flame, a palladium tube sealed to the apparatus, was subjected to a heavy discharge, and then removed by heating the palladium tube with a glowing spiral of platinum wire. When the apparatus was clean, no trace of argon, neon, or helium was obtained. Minute amounts of argon appearing in the earlier experiments were traced to minute leakage of air, due to a small amount of dirt in the barometric seal. Air was also found to leak through stopcocks which had every appearance of being trustworthy. It is considered doubtful by this author whether stopcocks can be trusted in dealing with such minute quantities of gases.

These results, therefore, are to be ranged with those of Strutt, obtained last year, against the view that helium and neon are obtained when due precautions are taken to avoid contamination. Merton's apparatus was subsequently handed over to Collie,[55] who used it, in conjunction with a cold charcoal apparatus, to demonstrate that uranium gives off, by bombardment with cathode rays, considerable amounts of nitrogen, helium, and neon, although none could be obtained from the uranium by heating. However interesting such observations may be, they seem confusing to the point at issue. Deliberately to put a radioactive source of helium into such an apparatus is simply to spoil the apparatus for the question it was designed to test. For, in the writer's experience, once helium has been used in a discharge apparatus, ever afterwards helium, of the order of magnitude under consideration, may be obtainable from that apparatus.

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[50] A. B. Wood, *Phil. Mag.*, 1914, [vi], **28**, 808; *A.*, 1915, ii, 5. Compare *Ann. Report*, 1912, 318.

[51] *Ann. Report*, 1913, 284.

[52] Sir J. J. Thomson, Romanes Lecture, 1914, p. 18.

[53] T. R. Merton, *Proc. Roy. Soc.*, 1914, [*A*], **90**, 549; *A.*, ii, 726.

[54] F. Soddy and T. D. Mackenzie, *ibid.*, 1908, [*A*], **80** 92.

[55] J. N. Collie, *ibid.*, 1914, [*A*], **90**, 554; *A.*, ii, 727.

In a paper[56] entitled "The Production of Neon and Helium by the Electric Discharge," fuller details are given of the experimental apparatus by which the previously published results, discussed at length last year, and some new ones, were obtained, together with a résumé of the results and a discussion of the sources of the gases in question. Many of these experiments also gave negative results, but the account deals mainly with those that gave positive results. Apparently, latterly, difficulty has been experienced in obtaining such large yields of helium and neon as formerly, and this is ascribed to differences in the interrupters employed with the coils. A wide diversity of apparatus was used. In some, transference of gas from the discharge apparatus to the testing apparatus was avoided. Electrodes of various metals were employed, and in many experiments helium and neon were found, in spite of all precautions to ensure the purity of the gas and to eliminate air-leakage. The absence of argon was considered to be an extremely delicate proof that the neon and helium found were not derived from the air.

New experiments with a silica-tube mercury arc apparatus, in which considerable quantities of helium and neon were found after running the arc in air, pointed to the atmosphere in this case as the source of the gases, for, with the apparatus water-jacketed, no helium or neon was obtained even after protracted running. Hydrogen, when introduced, disappeared rapidly during the discharge, leaving no gaseous residue.

Arguments are advanced against the helium and neon in the earlier experiments having been derived from leakage of air, by permeation through the walls of the discharge tubes, or by previous occlusion of the gases in the materials of the discharge tube, and negative results were obtained when old glasses were melted in a vacuum and when aluminium electrodes were dissolved. The authors disclaim the view that their experiments rigidly exclude the possible sources of the gases discussed, but conclude "that the trend of the results is towards conclusions which, if they turn out to be true, would be of very obvious importance." Clearly, however, the onus of proof now rests with them to show that these infinitesimal quantities of helium and neon have a real significance. It is noteworthy, also, that in some of these later experiments the quantities of the gases in question observed must have been extremely near the limit of detectability, for in criticism of Strutt's negative results, the authors state that they have found it necessary that the capillary tubes, used to detect the gases spectroscopically, must, to be sufficiently sensitive, be so fine that mercury can only be driven out of them by strong heating: yet the spectroscopic test for neon and helium is excessively delicate.

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[56] J. N. Collie, H. S. Patterson, and I. Masson, *Proc. Roy. Soc.*, 1914, [*A*], **91**, 30; *A.*, ii, 847.

Action of Radium on the Diamond: Chemical Actions.

In a record of various experiments, extending over a long term of years, on the action of radium on various substances, and especially on the diamond, some observations were made which indicate considerable differences between the diamond and other materials rendered radioactive by exposure to the radium emanation.[57] First may be mentioned the absence of any trace of radioactivity in a yellow, phosphorescent diamond, which during forty years had been used in a Crookes' tube to show the phosphorescence produced by cathode rays. No coloration was produced in a diamond exposed for six months to the β- and γ-rays from a sealed tube containing 15 milligrams of radium bromide, but, when subjected to the α-rays and emanation by being enclosed in a tube containing radium bromide for seventy-eight days, it acquired a bluish-green colour and an enduring radioactivity, comprising α- and β- and γ-rays. Such acquired radioactivity, which it would be natural to ascribe to radium-*D*, -*E*, and -*F*, proved extraordinarily enduring after drastic chemical treatment. Neither the colour nor the activity was affected by prolonged treatment with a hot mixture of fuming nitric acid and potassium chlorate, whereas lead glass which had been rendered active by being buried for a long period in a radium preparation lost nearly all the acquired activity by treatment with dilute nitric acid. Cutting the diamond into a brilliant completely removed both the activity and the colour.

Another difference between the diamond and a quartz crystal, for example, rendered active by prolonged contact with a radium preparation, was shown in the image produced when laid on a sensitive plate. The latter showed the ordinary image of geometric pattern, due to the superficial deposit of active matter and the equality of the intensity of the rays in all directions, studied by Rutherford. In the case of the diamond, however, the photographs suggested a special discharge of energy from the points and corners of the crystal. It is not explicitly recorded what precautions were taken against phosphorescent light emitted by the diamond to exclude it from contributing to the action.

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[57] Sir W. Crookes, *Phil. Trans.*, 1914, [*A*], **214**, 433.

With regard to the very interesting peculiarity shown by the diamond in retaining its activity after drastic chemical treatment, short of supposing a real stimulation of the diamond into radioactivity, which would be a phenomenon of an entirely new and revolutionary character, and is not suggested, possibly the surface of the diamond possesses for radium-*D* and its products a special attraction, analogous to that shown by palladium for polonium.[58] The subject opened out is new and very attractive.

During the year, the decomposition of ammonia,[59] the combination of hydrogen and oxygen,[60] and the reduction of carbon monoxide by hydrogen[61] under the influence of radium emanation have been studied. In the latter research, a diminution of volume of nearly 10 per cent. occurred after nineteen days, corresponding with a production of methane to the extent of 5 per cent., and ethane 0·12 per cent. When stopped at an earlier stage, traces of formaldehyde were found, and the conclusion is drawn that the reaction occurs in two stages, formaldehyde being an intermediate product.

FREDERICK SODDY.

[58] *Ann. Report*, 1913, 274.

[59] E. Wourtzel, *Compt. rend.*, 1914, **158**, 571 ; *A.*, ii, 238.

[60] O. Scheuer, *ibid.*, **159**, 423 ; *A.*, ii, 762.

[61] *Idem.*, *ibid.*, **158**, 1887 ; *A.*, ii, 649.

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ERRATUM.

Page 27, line 27, *for* "pure solvent and the solution" *read* "solution and the pure solvent."

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